Infrared excitation processes of C₂H₆ in comets

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(Received July 11, 2002; Revised February 12, 2003; Accepted February 18, 2003)

A time-dependent and line-by-line fluorescence model of the v_7 band of C_2H_6 has been constructed. Collisional (neutrals and electrons) and radiative excitation effects have been considered in the calculations of fluorescence efficiency factors (g-factors) of the C_2H_6 v_7 band. Since the lifetime of C_2H_6 is ~91,000 seconds at a heliocentric distance of 1 AU, C_2H_6 molecules far from the nucleus approach fluorescence equilibrium, while molecules within the contact surface should have a much colder rotational distribution due to collisional equilibration with the low temperature gases in that region. We would recommend using "single-cycle" fluorescence models for the analysis of v_7 band spectra taken with small apertures centered on the nucleus. We analyzed a v_7 band spectrum of comet Hale-Bopp (C/1995 O1) obtained at the IRTF with the CSHELL on 2 March, 1997 (R = 1.1 AU, $\Delta = 1.5$ AU) using a square aperture of 1,000 × 2,000 km, and constructed synthetic spectra to compare with the observation. We analyzed spatial brightness profiles of the ^RQ₀ sub-branch and found that the eastward profile is very well matched by the models, but the observed westward profile is clearly broader than the eastward profile suggesting asymmetric outflow and/or extended sources. We derived a C_2H_6 production rate of ~1.7±0.9 × 10²⁸ molec s⁻¹ from the inner coma region of the comet at the time of the observation.

1. Introduction

The v_7 band of C_2H_6 was detected at 3.3 microns during the observations of the bright comets Hyakutake (C/1996 B2) (Mumma et al., 1996), and Hale-Bopp (C/1995 O1) (Weaver et al., 1999; Dello Russo et al., 2001) at the NASA Infrared Telescope Facility (IRTF). Many parent molecules, such as CH₃OH, CH₃CN, HCN, H₂CO, H₂CS, H₂S, OCS, etc., have been successfully detected in the radio spectra of various recent comets. C2H6, like CH4 and C2H2, has no permanent electric dipole moment, and consequently no strong rotational transitions, and therefore, is inaccessible to radio observations. C₂H₆ cannot be observed in emission at ultraviolet wavelengths because it is predissociated by absorption of solar ultraviolet radiation before fluorescence can take place. C₂H₆ has strong rotational-vibrational bands in the infrared, and the ν_9 band of C₂H₆ at 12 microns has been used to investigate the atmospheres of Jupiter, Saturn, and Neptune (e.g., Kostiuk et al., 1987; Kostiuk et al., 1990; Livengood *et al.*, 1993). However, the v_7 band at 3.3 microns has not been detected in planetary spectra.

 C_2H_6 has a lifetime of ~91,000 seconds at 1 AU against dissociation by the ultraviolet radiation of a quiet sun (Huebner, 1992). The spatial brightness profile of C_2H_6 obtained by Weaver *et al.* (1999) indicates that the majority of C_2H_6 molecules were directly emitted from the nucleus of Hale-Bopp without significant extended sources. Recently, Dello Russo *et al.* (2001) derived a heliocentric dependence of C_2H_6 production rates for Hale-Bopp using extensive observational data, and confirmed that the all C_2H_6 was released from the nucleus, although a small fraction might be released from a distributed source. In this paper, we discuss the timedependent excitation processes of the v_7 band by solar infrared radiation, neutral and electron collisions, and investigate dominant excitation processes. A synthetic spectrum of the v_7 band as it would appear in the aperture used for our observations is constructed in order to be compared with the observed spectrum. We also analyze the spatial brightness profiles of C_2H_6 sub-branches by comparing them with model profiles. We derive a C_2H_6 production rate for Hale-Bopp using our calculated *g*-factors. Some of preliminary results were reported by Kim *et al.* (2000).

2. Observations

The observations of Hale-Bopp were made at IRTF on 2 March 1997 (UT), when the solar activity was low, using the Cryogenic Echelle Spectrometer (CSHELL) with a spectral resolving power of $\sim 20,000$. The spectrometer slit was 1" (spectral direction) \times 30" (spatial direction), which corresponds to $\sim 1100 \text{ km} \times 33,000 \text{ km}$ at the comet, and the nucleus was approximately centered in the 1" direction. The heliocentric and geocentric distances of the comet were ~ 1.1 AU and ~ 1.5 AU, respectively, and the geocentric and heliocentric velocities were ~ -24 km s⁻¹ and -14 km s⁻¹, respectively. In this paper, we use the observed intensities of the ${}^{R}Q_{0}$ and ${}^{R}Q_{1}$ sub-branches for the calculations of a rotational temperature and a C2H6 production rate at the time of the observations within the central region of the comet. We also use these intensities for the investigation of a spatial distribution of C_2H_6 up to 11,000 km from the nucleus. A detailed description of the observations was presented by Weaver *et al.* (1999), and will not be repeated here. C_2H_6 was one of 6 parent molecules, including H₂O, CH₄, C₂H₂,

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CO, and HCN, detected during the CSHELL observations at the IRTF.

3. Excitation Processes

3.1 Band models

The v_7 band of C_2H_6 is a perpendicular band of a symmetric top molecule. Cole et al. (1980) listed some line positions of the band, but they did not present line strengths, and ground state energies. Pine and Lafferty (1982) recorded the band with a spectral resolution of 0.0043 cm^{-1} in the 2870-3050 cm⁻¹ range and listed rotational quantum numbers, ground state energies, and experimentally obtained line intensities, along with line positions. However, the line list does not have line positions of sub-branches, such as ${}^{R}Q_{0}, {}^{R}Q_{1}$, etc., because the accumulated lines of the subbranches could not be resolved in their data. The Hitran2000 database contains ${}^{R}Q_{K}$ lines only for a limited spectral range (2970–3002 cm⁻¹), although it includes the ${}^{R}Q_{0}$ and ${}^{R}Q_{1}$ sub-branches. Therefore, we generated line positions, line strengths and ground state energies for all the lines of the v_7 band, so that the behavior of the whole band can be investigated in response to temperature changes in the coma and to the fluorescence process itself.

In order to calculate line positions and ground state energies, we used rotational constants of the v_7 band listed in Cole et al. (1980). For the calculations of line strengths, we considered Hönl-London (H-L) formulae, statistical weights including nuclear spin, and a rotational partition function including nuclear spin statistics, using formulae for a perpendicular band of a symmetric top molecule, similar to those used by Tokunaga and Varanasi (1976). We used an absolute band intensity of 351 cm⁻² atm⁻¹ at 295 K, a result from Dang-Nhu et al. (1984), since this value seems to be the most updated band intensity also used by Dello Russo et al. (2001), and therefore useful for comparison with the results of Dello Russo et al. A previously observed band intensity by Nyquist et al. (1957) is \sim 500 cm⁻² atm⁻¹ at 295 K, which was used by Mumma et al. (1996). Therefore, the derived g-factors and production rates may contain \sim 40% uncertainty arising from the uncertain band intensity alone. See Dello Russo et al. (2001) for detailed discussions on the band intensities. Einstein A coefficients for individual lines were calculated from line intensities using equation (2-17) of Penner (1959):

$$S_{lu} = \frac{c}{8\pi v_{lu}^2} \frac{N_l}{p} A_{u \to l} \frac{g_u}{g_l} \left(1 - \exp \frac{-h v_{lu}}{kT} \right), \qquad (1)$$

where, S_{lu} is the line intensity in a unit of cm⁻¹ atm⁻¹ at STP; subscripts *l* and *u* are the low and upper quantum states, respectively; *c* is the speed of light; v_{lu} is the frequency in Hz; N_l is the number of absorbers in cm⁻³; *p* is the atmospheric pressure in bar; $A_{u\to l}$ is the Einstein A coefficient in sec⁻¹; g_u and g_l are the statistical weights for upper and lower states, respectively; *h* is the Planck constant; *k* is the Boltzmann constant; and *T* is the temperature in Kelvin.

Before we calculate the fluorescence between the upper states of the ν_7 band and the ground states, we checked other fundamental bands and combination band intensities, which might influence the fluorescence excitation of the ν_7 band. We calculated rough fluorescence efficiencies (see Table 1) for the ν_5 fundamental band using a result of Dang-Nhu *et al.* (1984); and for the ν_8 , ν_6 , and ν_9 fundamental bands using band intensities listed in table 2 of Lii and Allinger (1992); and using the following formula:

Band g-factor =
$$S_{band}\eta/h\omega \,\mathrm{s}^{-1}$$
 molecule⁻¹, (2)

where S_{band} is the band intensity (cm² s⁻¹ molecule⁻¹), η is the solar radiation density (erg cm⁻³ Hz⁻¹), h is the Planck constant, and ω is the wavenumber (cm⁻¹) of the band centers. Equation (2) is valid when most of the molecular population is in the ground state. In this paper, we used a low resolution spectrum of Arvesen et al. (1969) for the infrared solar radiation density for convenience, because according to the high resolution spectra obtained by the ATMOS (Atmospheric Trace Molecule Spectroscopy) instrument on the Spacelab 3 mission, the solar infrared spectrum between 2800 and 3200 cm⁻¹ does not contain significant absorption features (Farmer and Norton, 1989). For the combination bands, we present only very rough band intensities (Table 1), which were derived by looking at a lab C₂H₆ spectrum of Pierson et al. (1956), since the quantitative values are not available in the literature.

There are more combination bands beyond 3000 cm^{-1} , but those band intensities are also very weak. There are no high pumping rates to the upper states of fundamental bands from the upper states of the combination bands, and no high pumping rates between the upper states of the fundamental bands, indicating that the fundamental band transitions dominate the excitation of C_2H_6 . We ignored over-tone transitions in our calculations, because the intensities of over-tone bands are less than a few percent of those of corresponding fundamental bands. As shown in Table 1, the ν_7 band has the largest excitation rate of any of the fundamental bands. The g-factor of the v_5 band is approximately 30% of that of the v_7 band, and therefore it may not be negligible. As will be discussed in the Subsection 3.3, the probed region by our IRTF observations was within the contact surface, and most of the observed C₂H₆ molecules are in LTE (local thermodynamic equilibrium). Since the majority of the C_2H_6 molecules are in the reservoir of ground states, the influence of the v_5 excitation on the v_7 state is negligible within the contact surface. In this paper, therefore, we ignored the v_5 band in the fluorescence calculations for the analysis of the IRTF spectra. However, in the outside regions of the contact surface, the excitation from the ground state to v_5 state should alter the LTE ground states into non-LTE states eventually influencing the v_7 state population. Ultimately, the derived g-factors of sub-branches listed in Table 3 may have an uncertainty of \sim 30% for the outside regions of the contact surface due to the neglect of the v_5 band in addition to the ~40% uncertainty from the uncertain band intensities discussed above. We defer complete calculations including the v_5 band and other weak bands, which require the inclusion of thousands of additional quantum states, to our future efforts.

3.2 Fluorescence calculations considering collisional and time-dependent effects

Before performing detailed fluorescence calculations, we briefly calculated the *g*-factors of sub-branches taking advantage of the selection rules of the v_7 band, and ignoring collisional effects to obtain approximate results, which are

Table 1. Band intensities and band fluorescence efficiency factors (g-factors).

Band (position)	Band intensity ($cm^2 s^{-1} molecule^{-1}$)	<i>g</i> -factor (s ^{-1} molecule ^{-1})
$\nu_7 \ (2995 \ \text{cm}^{-1})$	4.23×10^{-7}	4.65×10^{-4}
$\nu_5 \ (2895 \ \mathrm{cm}^{-1})$	1.38×10^{-7}	$1.50 imes 10^{-4}$
$v_8 (1472 \text{ cm}^{-1})$	$6.67 imes 10^{-8}$	4.46×10^{-5}
$\nu_6 (1379 \text{ cm}^{-1})$	1.99×10^{-8}	1.26×10^{-5}
$\nu_9 \ (821 \ cm^{-1})$	$3.79 imes 10^{-8}$	1.54×10^{-5}

$v_4 + v_{12} (1414 \text{ cm}^{-1})$ less than 3% of v_9 band
$v_4 + v_{11} (1747 \text{ cm}^{-1})$ less than 5% of v_9 band
$\nu_2 + \nu_9$, $2\nu_{12}$ (2218 cm ⁻¹) less than 5% of ν_9 band
$v_9 + v_{11}$ (2302 cm ⁻¹) less than 5% of v_9 band
$v_3 + v_6 \ (2368 \ cm^{-1}) \ about \ 5\% \ of \ v_9 \ band$
$v_2 + v_6 (2753 \text{ cm}^{-1}) \text{ about } 5\% \text{ of } v_9 \text{ band}$
$v_8 + v_{11}$ (2954 cm ⁻¹) less than 5% of v_9 band

Table 2. Absorption rates (sec⁻¹ molecule⁻¹) of ${}^{R}Q_{0} \rightarrow {}^{R}Q_{11}$ sub-branches results from approximate calculations presented in Appendix A.

	T = 70 K	T = 130 K	$T = 190 { m K}$	$T = 300 { m K}$
$^{R}Q_{0}$	3.6837×10^{-5}	2.7080×10^{-5}	2.2319×10^{-5}	1.7282×10^{-5}
$^{R}Q_{1}$	2.6203×10^{-5}	2.0557×10^{-5}	1.7392×10^{-5}	1.3758×10^{-5}
RQ_2	1.9700×10^{-5}	1.7392×10^{-5}	1.5423×10^{-5}	1.2673×10^{-5}
$^{R}Q_{3}$	1.5769×10^{-5}	1.6508×10^{-5}	1.5630×10^{-5}	1.3544×10^{-5}
RQ_4	7.8359×10^{-6}	1.0206×10^{-5}	1.0510×10^{-5}	$9.7569 imes 10^{-6}$
$^{R}Q_{5}$	4.1757×10^{-6}	7.1173×10^{-6}	8.1262×10^{-6}	8.1883×10^{-6}
$^{R}Q_{6}$	2.3992×10^{-6}	5.6095×10^{-6}	7.2210×10^{-6}	8.0225×10^{-6}
$^{R}Q_{7}$	8.5960×10^{-7}	2.8932×10^{-6}	4.2766×10^{-6}	5.3062×10^{-6}
$^{R}Q_{8}$	3.3182×10^{-7}	1.6895×10^{-6}	2.9181×10^{-6}	4.1011×10^{-6}
$^{R}Q_{9}$	1.3799×10^{-7}	1.1160×10^{-6}	2.2941×10^{-6}	3.7017×10^{-6}
${}^{R}Q_{10}$	3.5904×10^{-8}	4.8329×10^{-7}	1.2030×10^{-6}	2.2596×10^{-6}
${}^{R}Q_{11}$	1.0075×10^{-8}	2.3729×10^{-7}	7.2762×10^{-7}	1.6107×10^{-6}

presented in Appendix A. We present the detailed effects of collisions in Appendix B. From the brief calculations presented in Appendix A, we notice that we could roughly calculate g-factors of the sub-branches using line absorption intensities without detailed calculations of Einstein A coefficients for individual lines. These rough results have been guides for the following complicated time-dependent fluorescence calculations, in which a mistake in the calculations may result in a drastically different result.

Short-life molecules do not achieve fluorescence equilibrium during their lifetimes. Some long-life molecules, such as C_2H_6 , do not achieve the fluorescence equilibrium quickly, if they have strict selection rules. Although one can use the fluorescence equilibrium approximation in many cases, time-dependent fluorescence calculations are often necessary to analyze cometary spectra for short-life molecules or for long-life molecules having strict selection rules.

In principle, the fractional population, x_i , of the quantum states of molecules can be calculated by solving the evolution

equations of the quantum state populations. The temporal rate of the fractional population is given by,

$$dx_{i}/dt = -x_{i} \sum_{j} (A_{ij} + B_{ij}\eta_{ij} + C_{ij}) + \sum_{j} x_{j} (A_{ji} + B_{ji}\eta_{ji} + C_{ji}), \qquad (3)$$

where *i* and *j* are the upper and lower quantum states, respectively; *A* is the Einstein A coefficients for emission transitions; *B* is the Einstein B coefficient for absorption transitions; and *C* is the transition rate by collisions with neutrals or ions. Experimentally determined *C* for the C_2H_6 and H_2O collisions, and C_2H_6 and electrons/ions are not available in literature. Theoretical considerations of various collisional excitation rates used in this paper are presented in Appendix B. The first term in Eq. (3) represents the summation of outgoing population rates from the quantum state *i* to *j*, and the second term represents the summation of incoming population rates from the state *j* to *i*, wherever transitions are possible. Equation (3) can be expressed by a first

						Fig. 1(a)	Fig. 3(a)
	T = 20 K	T = 30 K	T = 40 K	T = 50 K	T = 60 K	T = 70 K	T = 70 K
	$t \sim 0 \sec$	$t \sim 0 \sec$	$t \sim 0 \sec$	$t \sim 0 \sec$	$t \sim 0 \sec$	$t \sim 0 \sec$	$t \sim 10^5 \text{ sec}$
$^{R}Q_{0}$	5.170×10^{-5}	4.542×10^{-5}	4.103×10^{-5}	3.7722×10^{-5}	$3.508 imes 10^{-5}$	3.2926×10^{-5}	8.2574×10^{-6}
$^{R}Q_{1}$	2.779×10^{-5}	2.822×10^{-5}	2.794×10^{-5}	2.7294×10^{-5}	2.655×10^{-5}	2.5767×10^{-5}	7.9050×10^{-6}
$^{R}Q_{2}$	1.150×10^{-5}	1.419×10^{-5}	1.568×10^{-5}	1.6529×10^{-5}	1.694×10^{-5}	1.7130×10^{-5}	7.4490×10^{-6}
$^{R}Q_{3}$	4.186×10^{-6}	7.065×10^{-6}	9.177×10^{-6}	1.0697×10^{-5}	$1.180 imes 10^{-5}$	1.2590×10^{-5}	6.8789×10^{-6}
$^{R}Q_{4}$	7.589×10^{-7}	$2.049 imes 10^{-6}$	3.417×10^{-6}	4.6767×10^{-6}	$5.777 imes 10^{-6}$	6.7124×10^{-6}	6.3012×10^{-6}
$^{R}Q_{5}$	1.133×10^{-7}	5.392×10^{-7}	1.188×10^{-6}	1.9244×10^{-6}	2.660×10^{-6}	3.3576×10^{-6}	5.6911×10^{-6}
$^{R}Q_{6}$	1.408×10^{-8}	1.351×10^{-7}	4.210×10^{-7}	8.3818×10^{-7}	1.331×10^{-6}	1.8560×10^{-6}	5.1182×10^{-6}
$^{R}Q_{7}$	8.364×10^{-10}	1.868×10^{-8}	8.922×10^{-8}	2.3128×10^{-7}	4.406×10^{-7}	7.0206×10^{-7}	4.5406×10^{-6}
$^{R}Q_{8}$	4.118×10^{-11}	2.401×10^{-9}	1.847×10^{-8}	$6.3399 imes 10^{-8}$	1.456×10^{-7}	2.6486×10^{-7}	4.0175×10^{-6}
$^{R}Q_{9}$	1.669×10^{-12}	2.906×10^{-10}	3.841×10^{-9}	1.8222×10^{-8}	$5.174 imes 10^{-8}$	1.0952×10^{-7}	3.5124×10^{-6}
${}^{R}Q_{10}$	3.226×10^{-14}	1.905×10^{-11}	4.659×10^{-10}	3.2042×10^{-9}	$1.171 imes 10^{-8}$	2.9810×10^{-8}	3.0625×10^{-6}
${}^{R}Q_{11}$	5.126×10^{-16}	1.164×10^{-12}	5.581×10^{-11}	5.7353×10^{-10}	2.726×10^{-9}	8.3680×10^{-9}	2.6686×10^{-6}
${}^{P}Q_{1}$	4.879×10^{-5}	4.290×10^{-5}	3.853×10^{-5}	3.5269×10^{-5}	$3.263 imes 10^{-5}$	3.0535×10^{-5}	8.2022×10^{-6}
$^{P}Q_{2}$	$3.839 imes 10^{-5}$	$3.640 imes 10^{-5}$	3.430×10^{-5}	3.2408×10^{-5}	3.072×10^{-5}	2.9250×10^{-5}	7.8221×10^{-6}
$^{P}Q_{3}$	1.826×10^{-5}	2.060×10^{-5}	2.161×10^{-5}	2.1919×10^{-5}	$2.188 imes 10^{-5}$	2.1663×10^{-5}	7.2693×10^{-6}
$^{P}Q_{4}$	$6.839 imes 10^{-6}$	$9.620 imes 10^{-6}$	1.141×10^{-5}	1.2590×10^{-5}	$1.333 imes 10^{-5}$	1.3806×10^{-5}	6.6916×10^{-6}
$^{P}Q_{5}$	2.271×10^{-6}	$4.478 imes 10^{-6}$	6.328×10^{-6}	7.7807×10^{-6}	$8.908 imes 10^{-6}$	9.7707×10^{-6}	6.0518×10^{-6}
$^{P}Q_{6}$	3.764×10^{-7}	1.219×10^{-6}	2.239×10^{-6}	3.2574×10^{-6}	$4.198 imes 10^{-6}$	5.0339×10^{-6}	5.4409×10^{-6}
$^{P}Q_{7}$	$5.139 imes 10^{-8}$	3.011×10^{-7}	7.408×10^{-7}	1.2853×10^{-6}	1.864×10^{-6}	2.4372×10^{-6}	4.8273×10^{-6}
$^{P}Q_{8}$	$5.834 imes 10^{-9}$	$7.098 imes 10^{-8}$	2.502×10^{-7}	5.3781×10^{-7}	$9.007 imes 10^{-7}$	1.3053×10^{-6}	4.2690×10^{-6}
$^{P}Q_{9}$	3.175×10^{-10}	$9.228 imes 10^{-9}$	$5.054 imes 10^{-8}$	1.4262×10^{-7}	$2.880 imes 10^{-7}$	4.7907×10^{-7}	3.7279×10^{-6}
${}^{P}Q_{10}$	1.427×10^{-11}	1.116×10^{-9}	9.969×10^{-9}	3.7570×10^{-8}	$9.196 imes 10^{-8}$	1.7524×10^{-7}	3.2449×10^{-6}
${}^{P}Q_{11}$	5.275×10^{-13}	1.266×10^{-10}	1.976×10^{-9}	1.0379×10^{-8}	$3.157 imes 10^{-8}$	$7.0275 imes 10^{-8}$	2.7958×10^{-6}
${}^{P}Q_{12}$	9.277×10^{-15}	7.783×10^{-12}	2.280×10^{-10}	1.7496×10^{-9}	$6.895 imes 10^{-9}$	1.8533×10^{-8}	2.3985×10^{-6}

Table 3. g-factors (sec⁻¹ molecule⁻¹) for ${}^{R}Q_{0} \rightarrow {}^{R}Q_{11}$ and ${}^{P}Q_{1} \rightarrow {}^{P}Q_{12}$ sub-branches results from time-dependent calculations presented in Subsection 3.2.

order linear differential equation:

$$d\mathbf{x}/dt = \mathbf{A}\mathbf{x},\tag{4}$$

where **A** is the matrix of the coefficients, and **x** is the vector of fractional populations. The coefficients in A are usually different from each other many orders of magnitude, and the equations, in principle, require a short time step (ex. $\sim A_{ii}^{-1}$) to be solved numerically. Traditionally this kind of "stiff" differential equations have been approximately solved by employing a numerical method developed by Gear (1971), and other improved methods listed in Press et al. (1992). Kim et al. (1990) developed a different method, which is presented below, to approximately solve the "stiff" differential equations for the fluorescence processes of the ultraviolet bands of S_2 . Hairer and Wanner (1996) revisited the "stiff" case, and developed a convenient computer code. We compared the S_2 result from the computer codes of Hairer and Wanner (Private communcation with E. Hairer, 1999) and the one from Kim et al. (1990); and we found that the differences between two results are found to be usually less than 1%. A significant advantage of the method of Kim et al. (1990) is to reduce the computing time for the calculations of the sizable matrix A in Eq. (4) more than a factor of 10

compared with the the methods of Gear (1971) or Hairer and Wanner (1996).

The outgassing rate of Hale-Bopp was at least 10 times of that of comet P/Halley. It is, therefore, expected that collisions among constituents should be important in the inner coma of Hale-Bopp. The ionopause or the "contact surface" of comet P/Halley was found to be approximately 4300 km from the nucleus by the Giotto spacecraft (Neubauer et al., 1986). Within the contact surface, there is essentially no magnetic field and electron and neutral temperatures are roughly the same, suggesting approximate LTE condition (Cravens, 1989). According to Cravens, the distance to the contact surface from the nucleus is proportional to the 0.75 power of gas production rate. Hence, the contact surface of Hale-Bopp should be located at \sim 4300 km \times 10^{0.75} = \sim 24,000 km from the nucleus. Since the slit size of our IRTF observations was approximately 1100 km × 33,000 km at the comet, the observed C2H6 emissions should be formed mostly within the contact surface, and therefore the observed C_2H_6 molecules are mostly in LTE.

We considered vibrational and rotational excitations by collisions with electrons or H_2O molecules. Pure-rotational transitions due to electron collisions can be ignored through-

	T = 80 K	T = 90 K	T = 100 K	$T = 110 { m K}$	T = 120 K
	$t \sim 0 \sec$				
$^{R}Q_{0}$	3.109×10^{-5}	$2.958 imes 10^{-5}$	2.824×10^{-5}	2.706×10^{-5}	2.603×10^{-5}
$^{R}Q_{1}$	2.501×10^{-5}	2.426×10^{-5}	2.359×10^{-5}	2.295×10^{-5}	2.233×10^{-5}
$^{R}Q_{2}$	1.717×10^{-5}	1.710×10^{-5}	1.697×10^{-5}	1.681×10^{-5}	1.662×10^{-5}
$^{R}Q_{3}$	1.315×10^{-5}	$1.355 imes 10^{-5}$	$1.382 imes 10^{-5}$	1.401×10^{-5}	1.412×10^{-5}
$^{R}Q_{4}$	$7.488 imes 10^{-6}$	8.143×10^{-6}	8.671×10^{-6}	$9.115 imes 10^{-6}$	9.481×10^{-6}
$^{R}Q_{5}$	$3.993 imes 10^{-6}$	4.566×10^{-6}	$5.071 imes 10^{-6}$	$5.514 imes 10^{-6}$	5.902×10^{-6}
$^{R}Q_{6}$	$2.382 imes 10^{-6}$	$2.890 imes 10^{-6}$	$3.370 imes 10^{-6}$	$3.812 imes 10^{-6}$	4.224×10^{-6}
$^{R}Q_{7}$	$9.985 imes 10^{-7}$	1.317×10^{-6}	1.642×10^{-6}	1.967×10^{-6}	$2.285 imes 10^{-6}$
$^{R}Q_{8}$	4.162×10^{-7}	$5.926 imes 10^{-7}$	$7.872 imes 10^{-7}$	$9.931 imes 10^{-7}$	1.206×10^{-6}
$^{R}Q_{9}$	1.929×10^{-7}	3.003×10^{-7}	4.282×10^{-7}	5.723×10^{-7}	7.293×10^{-7}
${}^{R}Q_{10}$	$6.040 imes 10^{-8}$	1.051×10^{-7}	1.641×10^{-7}	2.369×10^{-7}	3.214×10^{-7}
${}^{R}Q_{11}$	$1.950 imes 10^{-8}$	$3.779 imes 10^{-8}$	$6.437 imes 10^{-8}$	$9.960 imes 10^{-8}$	1.436×10^{-7}
$^{P}Q_{1}$	2.881×10^{-5}	2.734×10^{-5}	2.606×10^{-5}	2.495×10^{-5}	2.397×10^{-5}
$^{P}Q_{2}$	$2.793 imes 10^{-5}$	$2.681 imes 10^{-5}$	$2.578 imes 10^{-5}$	$2.487 imes 10^{-5}$	2.404×10^{-5}
$^{P}Q_{3}$	$2.135 imes 10^{-5}$	$2.097 imes 10^{-5}$	$2.060 imes 10^{-5}$	2.021×10^{-5}	1.981×10^{-5}
$^{P}Q_{4}$	1.409×10^{-5}	1.425×10^{-5}	1.432×10^{-5}	1.433×10^{-5}	1.429×10^{-5}
$^{P}Q_{5}$	1.043×10^{-5}	$1.094 imes 10^{-5}$	1.132×10^{-5}	1.160×10^{-5}	1.182×10^{-5}
$^{P}Q_{6}$	$5.755 imes 10^{-6}$	$6.382 imes 10^{-6}$	$6.905 imes 10^{-6}$	7.357×10^{-6}	7.740×10^{-6}
$^{P}Q_{7}$	$2.978 imes 10^{-6}$	$3.480 imes 10^{-6}$	$3.934 imes 10^{-6}$	4.342×10^{-6}	4.705×10^{-6}
$^{P}Q_{8}$	1.726×10^{-6}	2.145×10^{-6}	2.551×10^{-6}	2.933×10^{-6}	3.295×10^{-6}
$^{P}Q_{9}$	$7.039 imes 10^{-7}$	$9.524 imes 10^{-7}$	1.213×10^{-6}	1.479×10^{-6}	1.744×10^{-6}
${}^{P}Q_{10}$	2.853×10^{-7}	$4.178 imes 10^{-7}$	$5.680 imes 10^{-7}$	7.304×10^{-7}	$9.009 imes 10^{-7}$
${}^{P}Q_{11}$	1.287×10^{-7}	$2.065 imes 10^{-7}$	$3.018 imes 10^{-7}$	4.118×10^{-7}	$5.339 imes 10^{-7}$
${}^{P}Q_{12}$	$3.915 imes 10^{-8}$	$7.033 imes 10^{-8}$	1.128×10^{-7}	1.665×10^{-7}	2.301×10^{-7}

Table 3. (continued).

out the coma because the collisional excitation rate is proportional to the electric dipole moment (Dickinson et al., 1977) and C₂H₆ has no permanent electric dipole moment. Purerotational transitions in the ground rotational states induced by collisions with H₂O determine the rotational state populations of the C₂H₆ molecules within the contact surface. As shown in detail in Appendix B, these collisional rotational excitation rates are equal to or greater than infrared fluorescence excitation rates from the ground states within the contact surface. Therefore, we can use LTE distributions for the ground rotational states within the contact space. This allows us to use the following "single-cycle" fluorescence equation, which is equation (1) of Kim et al. (1990), for the calculations of the upper level population of the v_7 band of C₂H₆ within the contact surface, because the LTE ground state populations cannot be changed by the infrared fluorescence excitations:

$$x_i^1 = \frac{\sum\limits_{j} B_{ji} \eta_{ji} x_j^o}{\sum\limits_{i} A_{ij}},$$
(5)

where x_i^1 is the fractional number density for the upper rotational state, *i*, of the v_7 band, and x_j^o is the initial fractional number density for the rotational state, *j*, of the ground state of the v_7 band. Local temperatures should determine x_j^o in LTE condition. Then, intensities for the "single-cycle" excitations, can be calculated by using the following relation:

$$I_{\nu} = N x_i^1 A_{ij} h \nu, \tag{6}$$

where N is the total column density of C_2H_6 , and v is the frequency in Hz.

Radiationless vibrational deexcitations by neutrals are only important very close to the nucleus, and are generally negligible throughout the coma. Vibrational excitations by electrons are thought to be negligible in inner coma regions, but they may not be negligible near the contact surface. These discussions on the collisional effects are presented in detail in Appendix B.

Beyond the contact surface, the ground rotational state populations are not only determined by collisions. Since the neutral collisions become scarce, the fluorescence cascades from the upper states should significantly alter the Boltzmann distribution of the ground state populations. As we discussed in Appendix B, it is not very clear at what distance the collisional effects become negligible compared with the fluorescence cascades, because the rotational collision cross-sections between C_2H_6 and H_2O have not been experimentally determined. The progress of fluorescence as the cometary gases expand in the region where the collisions are negligible can be described with a modified formula from

	Fig. 1(b)	Fig. 2(a)	Fig. 2(b)		Fig. 3(b)
	$T = 130 { m K}$	$T = 130 { m K}$	$T = 130 { m K}$	T = 140 K	$T = 300 { m K}$
	$t \sim 0 \sec$	$t \sim 2000 m sec$	$t \sim 4000 m ~sec$	$t \sim 0 \sec$	$t \sim 10^{+5} m sec$
RQ_0	2.5111×10^{-5}	1.9141×10^{-5}	1.8933×10^{-5}	2.427×10^{-5}	7.9050×10^{-6}
$^{R}Q_{1}$	2.1773×10^{-5}	1.6847×10^{-5}	1.6847×10^{-5}	2.124×10^{-5}	7.7116×10^{-6}
RQ_2	1.6418×10^{-5}	1.3931×10^{-5}	1.4159×10^{-5}	1.620×10^{-5}	7.3937×10^{-6}
$^{R}Q_{3}$	1.4186×10^{-5}	1.1298×10^{-5}	1.1484×10^{-5}	1.421×10^{-5}	7.0136×10^{-6}
RQ_4	9.7777×10^{-6}	8.1400×10^{-6}	8.5753×10^{-6}	1.002×10^{-5}	6.5721×10^{-6}
$^{R}Q_{5}$	6.2425×10^{-6}	5.8783×10^{-6}	6.3088×10^{-6}	6.536×10^{-6}	6.1008×10^{-6}
RQ_6	4.5945×10^{-5}	4.0299×10^{-5}	4.3685×10^{-6}	$4.933 imes 10^{-6}$	5.6116×10^{-6}
$^{R}Q_{7}$	2.5906×10^{-6}	2.4510×10^{-6}	2.8393×10^{-6}	$2.885 imes 10^{-6}$	5.1231×10^{-6}
$^{R}Q_{8}$	1.4186×10^{-6}	1.5706×10^{-6}	1.8394×10^{-6}	1.630×10^{-6}	4.6380×10^{-6}
$^{R}Q_{9}$	8.9484×10^{-7}	9.0521×10^{-7}	1.0876×10^{-6}	1.066×10^{-6}	4.1612×10^{-6}
${}^{R}Q_{10}$	4.1681×10^{-7}	4.7140×10^{-7}	6.2584×10^{-7}	$5.208 imes 10^{-7}$	3.7072×10^{-6}
${}^{R}Q_{11}$	1.9576×10^{-7}	2.6735×10^{-7}	3.5338×10^{-7}	$2.553 imes 10^{-7}$	3.2767×10^{-6}
$^{P}Q_{1}$	2.3086×10^{-5}	1.8906×10^{-5}	1.8857×10^{-5}	$2.230 imes 10^{-5}$	7.8981×10^{-6}
$^{P}Q_{2}$	2.3301×10^{-5}	1.7779×10^{-5}	1.7600×10^{-5}	$2.261 imes 10^{-5}$	7.6494×10^{-6}
$^{P}Q_{3}$	1.9438×10^{-5}	1.5057×10^{-5}	1.5071×10^{-5}	$1.907 imes 10^{-5}$	7.3108×10^{-6}
$^{P}Q_{4}$	1.4228×10^{-5}	1.2092×10^{-5}	1.2307×10^{-5}	1.413×10^{-5}	6.8920×10^{-6}
$^{P}Q_{5}$	1.1975×10^{-5}	9.5565×10^{-6}	9.7293×10^{-6}	$1.209 imes 10^{-5}$	6.4387×10^{-6}
$^{P}Q_{6}$	8.0640×10^{-6}	6.7262×10^{-6}	7.0966×10^{-6}	$8.335 imes 10^{-6}$	5.9502×10^{-6}
$^{P}Q_{7}$	5.0312×10^{-6}	4.7486×10^{-6}	5.1051×10^{-6}	$5.318 imes 10^{-6}$	5.4485×10^{-6}
$^{P}Q_{8}$	3.6264×10^{-6}	3.1883×10^{-6}	3.4626×10^{-6}	$3.934 imes 10^{-6}$	4.9462×10^{-6}
$^{P}Q_{9}$	2.0032×10^{-6}	1.9003×10^{-6}	2.2057×10^{-6}	2.256×10^{-6}	4.4625×10^{-6}
${}^{P}Q_{10}$	1.0752×10^{-6}	1.1934×10^{-6}	1.4007×10^{-6}	$1.250 imes 10^{-6}$	3.9843×10^{-6}
${}^{P}Q_{11}$	6.6509×10^{-7}	6.7442×10^{-7}	8.1262×10^{-7}	8.020×10^{-7}	3.5352×10^{-6}
${}^{P}Q_{12}$	3.0321×10^{-7}	3.4398×10^{-7}	4.5786×10^{-7}	3.841×10^{-7}	3.1088×10^{-6}

Table 3. (continued).

Eq. (3),

$$dx_{i}/dt = -x_{i} \sum_{j} (A_{ij} + B_{ij}\eta_{ij}) + \sum_{j} x_{j} (A_{ji} + B_{ji}\eta_{ji}),$$
(7)

where A_{ij} and A_{ji} are the Einstein A coefficients for emission transitions, and $B_{ij}\eta_{ij}$ and $B_{ji}\eta_{ji}$ are for absorption transitions, wherever possible (For example, $B_{ij}\eta_{ij}$ is not applicable or negligible in the upper states of the ν_7 band).

In the process of applying the method of Gear (1971), there is no semi-steady state or fluorescence cycle, but Kim *et al.* (1990) used the excitation time as a time step or a cycle for convenience. A disadvantage of Kim *et al.*'s method is, therefore, that one cannot use smaller time steps than the excitation time, whereas an advantage is that the computer code is significantly simpler (see IMSL Fortran subroutines for the Gear's method; and the other methods in Press *et al.* (1992) for comparisons), and required computing time is considerably shorter than others. In this paper, we utilized the equations of Kim *et al.*, and used the excitation time of the v_7 band of C₂H₆ as a time step, which is approximately 2000 seconds, an inverse of the *g*-factor of the v_7 band shown in Table 1. The initial upper level population is expressed by Eq. (5). The first modified ground state fractional density is then given by:

$$x_{j}^{1} = x_{j}^{0} - x_{j}^{0} \frac{\sum_{i} A_{ij} x_{i}^{1}}{\sum_{i} B_{ji} \eta_{ji}} + \frac{\sum_{i} A_{ij} x_{i}^{1}}{\sum_{i} B_{ji} \eta_{ji}},$$
(8)

The third term on the right side represents the number of transitions from all *i* levels of the upper states to level *j* of the ground states during the first cycle, in which the transitions into the ground states are balanced by transitions out of the ground states. The second term on the right side represents upward transitions, arbitrarily apportioned among the level *i* in proportion to the initial population. In the second term, x_j^0 was inadvertently omitted in Kim *et al.* (1990), and the first term should be x_j^0 , which was x_i^0 in Kim *et al.* The next upper state population for the second cycle is given by,

$$x_{i}^{2} = \frac{\sum_{j} B_{ji} \eta_{ji} x_{j}^{1}}{\sum_{j} A_{ij}}.$$
(9)

This calculation is continued for successive time steps. The Eqs. (5), (8), and (9) correspond to equations. (1), (3), and



Fig. 1. (a) A model spectrum of the ν_7 band of C₂H₆ at 70 K LTE distribution for the ground state. Each sub-branch has been designated at bandhead positions, which are slightly leftward of the centers of sub-branches. (b) A model spectrum of the ν_7 band at 130 K LTE distribution for the ground state. Numerous weak lines under the strong PQ_K and RQ_K sub-branches are attributed to other sub-branches (PP , PP , PR , and RR). The spectra in Figs. 1(a) and (b) are single-cycle fluorescence models as discussed in the main text.

(4) of Kim *et al.*, respectively. We considered rotational states up to J = 32 and K = 32, and the total number of lines are 3012 for the v_7 band. For handling the calculations, we should consider i + j = 1122 states. If we use a conventional Gaussian elimination method to solve Eq. (7) for fluorescence equilibrium case, it is equivalent to solving an inversion of a 1122×1122 matrix, and obviously it requires a significant computing time.

The resultant spectra of the v_7 band immediately after the initiation of the excitations of the 70 K and 130 K ground state distributions are presented in Figs. 1(a) and 1(b), respectively. Model spectra of the v_7 band were calculated using Eq. (6), and then we convolved the model spectra with a triangular slit function with FWHM = 0.15 cm⁻¹, which is the approximate resolution of the CSHELL observations. Numerous weak lines in the figures under the strong PQ_K and RQ_K sub-branches are attributed to other sub-branches (PP , RP , PR , and RR). Figures 2(a) and 2(b) show synthetic spectra of the v_7 band, 2000 and 4000 seconds after the excitations, respectively, with an initial temperature of 130 K. In Figs. 1(b), 2(a), and 2(b), propagations of excited popula-

tions to upper rotational levels can be seen. Figures 3(a) and 3(b) show synthetic spectra after $\sim 10^5$ seconds (after 75 cycles) with initial ground state temperatures 70 K and 300 K, respectively. Note that significant difference in the rotational features is shown between Figs. 1(a) and (b) for the case of 60 K initial difference (70 K vs 130 K), but the spectral features shown in Figs. 3(a) and 3(b) are similar in spite of 230 K difference (70 K vs 300 K) in the initial temperatures. The similarity between Figs. 3(a) and 3(b) indicates that after $\sim 10^5$ seconds the ν_7 band is in near fluorescent equilibrium almost independent of the initial temperatures. Since the lifetime of C_2H_6 is ~91,000 seconds at a heliocentric distance of 1 AU, the v_7 band spectrum just before C_2H_6 dissociation should be similar to the spectra in Figs. 3(a) and 3(b). In Table 3, we present g-factors of ${}^{R}Q_{0}$ through ${}^{R}Q_{11}$ and ${}^{P}Q_{1}$ through ${}^{P}Q_{12}$ corresponding to Figs. 1(a), 1(b), 2(a), 2(b), 3(a), and 3(b). Dello Russo et al. (2001) derived gfactors for ${}^{P}Q_{K}$ $(K = 1 \rightarrow 4)$ and ${}^{R}Q_{K}$ $(K = 0 \rightarrow 4)$ sub-branches, which are approximately consistent with our values with $\sim 10\%$ difference. The difference should be due to the fact that they did not perform time-dependent calcula-



Fig. 2. (a) A model spectrum of the v_7 band ~2000 seconds after the excitations with an initial temperature of 130 K. (b) A model spectrum of the v_7 band ~4000 seconds after the excitations with an initial temperature of 130 K. In Figs. 1(b), 2(a), and 2(b), the propagations of the populations from low rotational quantum states to high rotational quantum states can be seen, as the time-dependent fluorescence proceeds.

tions and we used a "single cycle" fluorescence, as described previously.

In Fig. 4, we present the spatial brightness profiles of Hale-Bopp for ${}^{R}Q_{0}$ (diamond), ${}^{R}Q_{1}$ (cross), the continuum near the C₂H₆ sub-branches (solid line), and the ${}^{R}Q_{0}/{}^{R}Q_{1}$ ratio (asterisk). We found that the ${}^{R}Q_{0}/{}^{R}Q_{1}$ ratio is approximately 1.55 within ± 2 arcsec from the nucleus. For $\rho \geq +2''$ (celestial east; ρ is the projected distance from the nucleus), the ratio becomes noisy, but it seems less than or equal to 1.5. For $\rho \leq -2''$ (celestial west), the ratio also becomes noisy, but it seems larger than ~ 1.5 . The ratio should approach 1 far from the nucleus, as the temperatures go up, and the multistep fluorescence cycle makes the ratio approach 1, as shown in Figs. 3(a) and 3(b). However, the observed ratios far from the nucleus are too noisy to measure this effect. We estimate that the relative uncertainties of the observed intensities of the ${}^{R}Q_{0}$ and ${}^{R}Q_{1}$ sub-branches are ~20%. Using the intensities and the error bars, and utilizing ${}^{R}Q_{0}$, ${}^{R}Q_{1}$ model intensities listed in Table 3, we derived a conservative temperature range, which should be less than 130 K within ± 2 arcsec from the nucleus. Dello Russo et al. (2001) derived rotational temperatures of 78 and 134 K for C₂H₆ spectra obtained on 24 February and 8 April, 1997 (UT), respectively, while our observations were done on 2 March, 1997 (UT). Our derived temperature range is broader than the results of Dello Russo *et al.*, because we used only two lines (i.e., ${}^{R}Q_{0}$ and ${}^{R}Q_{1}$ sub-branches), whereas Dello Russo *et al.* usually used more than several lines to derive rotational temperatures.

We derive a C_2H_6 production rate of $\sim 1.7 \pm 0.9 \times 10^{28}$ molec s⁻¹ within ±2 arcsec from the nucleus using the *g*-factor of $^{R}Q_0$ assuming 70 K and an outflow velocity of 0.8 km s⁻¹. Since we were not able to derive an accurate temperature as mentioned above, we assumed 70 K, which is an approximate average value from various temperatures presented in table 4 of Dello Russo *et al.* (2001). However, the assumed temperature causes additional uncertainty in the derived production rate due to the difference in the *g*-factors. Dello Russo *et al.* derived $\sim 2 \times 10^{28}$ molec s⁻¹ on 6 April, 1997 (UT) near the central region of the coma as shown in their Fig. 5. They also derived C₂H₆ production rates of $4 \sim 8 \times 10^{28}$ molec s⁻¹ far from the nucleus on the same day. We were not able to derive accurate C₂H₆ production rates far from the nucleus because of poor signals of the C₂H₆



Fig. 3. (a) A model spectrum after $\sim 10^5$ seconds (after 75 cycles) with an initial ground state temperature of 70 K. (b) A model spectrum after $\sim 10^5$ seconds (after 75 cycles) with an initial ground state temperature of 300 K. Rotational features shown in Figs. 3(a) and 3(b) are similar in spite of significant initial temperature difference. The similarity between Figs. 3(a) and 3(b) indicates that after $\sim 10^5$ seconds the ν_7 band is in near fluorescent equilibrium almost independent of the initial temperatures.

lines.

According to a spatially resolved C_2H_6 distribution presented in figure 3 of Weaver *et al.* (1999), most of the C_2H_6 molecules seem to be released from the nucleus without having extended sources. Assuming a spherical geometry and an outflow velocity of 1 km s⁻¹, we found that ~85% of the molecules are within 1500 km from the nucleus in the square aperture of 1000 km × 2000 km. In Fig. 5, we present spatial brightness profiles for the ^{*R*} Q₀ sub-branch (diamond), and a Haser model (solid line), in which we used a C₂H₆ lifetime of 91,000 seconds assuming C₂H₆ as a parent molecule without extended sources. The Haser model was convolved with a point-spread-function obtained from observations of a star (see figure 3 of Weaver *et al.*, 1999). The comet's apparent phase angle as seen from the observer's location at the time of the observation was ~42 deg.

As seen in Fig. 5, the observed eastward profile is very well matched with the Haser model, but the observed westward profile is clearly broader than the observed eastward profile. On the westward profile, the deviation from the model apparently starts approximately at -1.5 arcsec from

the nucleus, and it is about 30% at -2 arcsec. The deviation grows to $\sim 100\%$ near -4 arcsec, and beyond this point the noise becomes high, but the 100% deviation seems to be approximately maintained. The quality of the background subtraction becomes increasingly important at large cometocentric distances and the observations are less trustworthy there. However, we believe that the asymmetry is a true structure as similar asymmetries are observed in other species (see figure 3 of Weaver et al., 1999), and a spherically symmetric model cannot be expected to match this asymmetry. Possibilities include asymmetric outflow (e.g., jets) from the nucleus and/or extended sources. The asymmetric outflows have also been reported in figure 4 of Dello Russo et al. (2001). Dello Russo *et al.* also found that the spatial distribution of C_2H_6 molecules in the coma was consistent with all ethane being released directly from the nucleus, although possibility that a small fraction was released from a distributed source cannot be excluded. We clearly need information on the structure of the asymmetric outflow and extended sources at the time of observations in order to account for the asymmetry.



Fig. 4. Spatial brightness profiles of Hale-Bopp for ${}^{R}Q_{0}$ (diamond), ${}^{R}Q_{1}$ (cross), the continuum near the C₂H₆ sub-branches (solid line), and the ${}^{R}Q_{0}{}^{/R}Q_{1}$ ratio (asterisk). The comet's apparent phase angle as seen from the observer's location at the time of the observation was ~42 deg.



Fig. 5. Spatial brightness profiles of Hale-Bopp for ${}^{R}Q_{0}$ (diamond), and the single-cycle fluorescence model (solid line). The comet's apparent phase angle as seen from the observer's location at the time of the observation was \sim 42 deg.

4. Conclusions

We have discussed the time-dependent excitation process of the v_7 band of C_2H_6 by solar infrared radiation, neutral collisions, and electron collisions in detail. We conclude that the rotational populations of C₂H₆ molecules in the ground vibrational state should be in LTE within the contact surface (i.e., within \sim 24,000 km from the nucleus of Hale-Bopp), and that C₂H₆ molecules far from the nucleus (i.e., well beyond the contact surface) should be nearly in fluorescent equilibrium. We presented models of time-dependent fluorescence processes beyond the contact surface. We found that a "single-cycle" fluorescence model for the v_7 band is appropriate for the analysis of spectra taken within the contact surface, or taken from small apertures centered on the inner comae of cometary nuclei. The models also show that after ${\sim}10^5$ seconds (*photo-dissociation time of C_2H_6 at 1 AU) spectral features of the ν_7 band are in near fluorescent equilibrium almost independent of initial temperatures of C_2H_6 . We calculated *g*-factors of the sub-branches of the v_7 band, and compared our best model to the data taken on 2 March, 1997 (UT) from Comet Hale-Bopp and derived a production rate of $1.7 \pm 0.9 \times 10^{28}$ molec s⁻¹ from the inner coma region (within +/-2,000 km from the nucleus). We also analyzed the observed spatial brightness profiles of the $^{R}Q_{0}$ sub-branch and found an asymmetric outflow between the eastward and westward profiles suggesting asymmetric outflow and/or extended sources.

Acknowledgments. Drs. H. Weaver and G. Chin provided valuable comments on this manuscript. A special thank to Dr. Weaver who provided observational data for Hale-Bopp presented in Figs. 4 and 5. Two anonymous referees provided valuable comments, which greatly improved the manuscript. SJK would like to acknowledge financial support from the Korean Science and Engineering Foundation (KOSEF R14-2002-043-01000-0).

Appendix A. Approximate Fluorescence Calculations Neglecting Collisional Effects

We approximately calculate the *g*-factors of sub-branches taking advantage of the selection rules of the v_7 band in order to check the detailed calculations presented in Subsection 3.2 for the outside region of the contact surface where collisional effects are negligible. The selection rules for a perpendicular band of a symmetric top molecule are given by:

> ^{*P*} P_K branch: $\Delta J = -1$, $\Delta K = -1$; ^{*R*} P_K branch: $\Delta J = -1$, $\Delta K = +1$; ^{*P*} Q_K branch: $\Delta J = 0$, $\Delta K = -1$; ^{*R*} Q_K branch: $\Delta J = 0$, $\Delta K = +1$; ^{*P*} R_K branch: $\Delta J = +1$, $\Delta K = -1$; and ^{*R*} R_K branch: $\Delta J = +1$, $\Delta K = +1$.

Here, we ignore collisions to obtain approximate values, and will discuss the effects of collisions in Appendix B in detail. Because the selection rules are very strict for the *J* and *K* states, there is a semi-closed system in the fluorescence process. For example, the sub-branches connecting to the upper K' = 1 states are only ${}^{R}Q_{0}$, ${}^{R}P_{0}$, ${}^{R}R_{0}$, ${}^{P}Q_{2}$, ${}^{P}P_{2}$, and ${}^{P}R_{2}$. If we write a steady-state equation considering only these sub-branch transitions, and ignoring fluorescence

propagations to upper/lower J and K states:

$$\begin{aligned} x_{J'=all,K'=1} \left[\sum_{J''=0} A_{J'=all,J''=all,K'=1,K''=0} \\ &+ \sum_{J''=0} A_{J'=all,J''=all,K'=1,K''=2} \right] \\ &= \sum_{J''=0} S_{J''=all,J'=all,K'=1,K''=0} \eta / h\omega \\ &+ \sum_{J''=0} S_{J''=all,J'=all,K'=1,K''=2} \eta / h\omega. \end{aligned}$$
(A.1)

Here *x* is the fractional population for the J' = all, K' = 1 state, *A* is the Einstein A coefficient for $J' \rightarrow J''$, $K' \rightarrow K''$ transitions, and *S* is the line intensity in a unit of cm² s⁻¹ molec⁻¹ for $J'' \rightarrow J'$, $K'' \rightarrow K'$ transitions. The first and second terms on the left side of Eq. (A-1) are the summed emission rates for the ${}^{R}Q_{0}$, ${}^{R}P_{0}$, ${}^{R}R_{0}$, and the ${}^{P}Q_{2}$, ${}^{P}P_{2}$, ${}^{P}R_{2}$ sub-branches, respectively. The first and second terms on the right side of Eq. (A.1) are the summed absorption rates for the ${}^{R}Q_{0}$, ${}^{R}P_{0}$, ${}^{R}R_{0}$ and the ${}^{R}Q_{2}$, ${}^{P}P_{2}$, ${}^{P}R_{2}$ sub-branches, respectively. The first and second terms on the right side of Eq. (A.1) are the summed absorption rates for the ${}^{R}Q_{0}$, ${}^{R}P_{0}$, ${}^{R}R_{0}$ and the ${}^{R}Q_{2}$, ${}^{P}P_{2}$, ${}^{P}R_{2}$ sub-branches, respectively. The unit of Eq. (A.1) is sec⁻¹ molec⁻¹.

Using the line-by-line band model of the v_7 band mentioned previously, we calculated the right hand side of Eq. (A.1), which is 0.94×10^{-4} s⁻¹ molec⁻¹ for a 130 K ground state Boltzmann distribution for example. (We derived a conservative value for the rotational temperature range < 130 K from observed ${}^{R}Q_{0}$ and ${}^{R}Q_{1}$ intensities, as discussed later in the main text. We also present models for the 20-300 K range in Table 3.) The Einstein A coefficient is proportional to the H-L factor, which is the line intensity strictly depending on rotational quantum numbers. The H-L factors of ${}^{R}Q_{0} + {}^{P}Q_{2}$, ${}^{R}P_{0} + {}^{P}P_{2}$, and ${}^{R}R_{0} + {}^{P}R_{2}$ sub-branches are approximately 0.5, 0.25, and 0.25, respectively, for high J, K states. Therefore, the g-factor of the ${}^{R}Q_{0}$ sub-branch is $0.94 \times 10^{-4} \times 0.25 = 2.35 \times 10^{-5} \text{ s}^{-1} \text{ molec}^{-1}$ at 130 K. We also directly calculated the ${}^{R}Q_{0}$ absorption rate using the first term on the right side of Eq. (A.1), and obtained $2.69 \times 10^{-5} \text{ s}^{-1} \text{ molec}^{-1}$ at 130 K, which is similar to the above emission rate.

We also calculated absorption (or excitation) rates for ${}^{R}Q_{0}$ through ${}^{R}Q_{11}$ for 50 K, 70 K, 130 K, 190 K, and 300 K, using the line-by-line model and Eq. (2). We used line intensities, S_{line}, instead of a band intensity, S_{band}, and present the results in Table 2. As seen in this table, the absorption rates of ${}^{R}Q_{0}$ sub-branches are roughly the same as the values derived in the previous paragraph within a factor of two.

Appendix B. Collisional Effects

We consider vibrational and rotational excitations by electron and H_2O collisions in detail below. In order to calculate the collisional excitation rates, it is necessary to estimate neutral and electron densities in cometary comae. The neutral density is expected to be high when the gas production rate of a comet is higher than those of normal comets. Here, we assume that the neutral density is proportional to the gas production rate. Since the gas production rate of Hale-Bopp was ~10 times greater than that of P/Halley, we assume that the neutral density of Hale-Bopp is 10 times of that of P/Halley. Using the H_2O number density of P/Halley.

presented in figure 1 of Krankowsky et al. (1986), the H₂O density of Hale-Bopp at the nucleus surface is estimated to be $\sim 10^{13}$ molec cm⁻³, and at the contact surface it is $\sim 5 \times 10^5$ molec cm^{-3} . It is expected that within the contact surface the pure-rotational excitations in the ground states of the v_7 band are controlled by H₂O collisions. Unfortunately, however, no rotational excitation rates by collisions between C₂H₆ and H₂O are reported in the literature. With the absence of the rate data, we considered adopting CO-H₂O rotational excitation cross-sections obtained by Green (1993; and private communications, 1992) for the C₂H₆-H₂O rotational excitation cross-sections. The CO data are attractive to us for the substitution of C_2H_6 , since CO has an unusually low electric dipole moment among diatomic molecules, and the molecular weight of CO is similar to that of C₂H₆. However, this adoption is not proper because CO is a diatomic molecule having a rotational quantum number J, whereas C₂H₆ is a symmetric-top polyatomic molecule having two rotational quantum numbers J and K. There is no known method to extrapolate J-dependent cross-sections to J, Kdependent cross-sections (private communications with Dr. D. Flower, 1998). If we blindly adopt the J-dependent crosssections of CO for C₂H₆ assuming that the summation of all K cross-sections of C_2H_6 at a certain J is equal to a crosssection of CO at a J, the excitation rates at the contact surface are roughly $10^{-5} \sim 10^{-6} \text{ s}^{-1}$. Here, we considered twenty strong K transitions for a J state, assuming the same cross-sections for all the twenty K states. As shown in Table 3. the g-factors of the sub-branches of C₂H₆ are in a range of $3.8 \times 10^{-5} - 1.7 \times 10^{-9} \text{ s}^{-1}$, and the *g*-factor of a line transition is expected to be less than these rates. From the above comparison between the collisional rotational excitation rates (i.e., $10^{-5} \sim 10^{-6} \text{ s}^{-1}$) and the fluorescence rates (i.e., $3.8 \times 10^{-5} - 1.7 \times 10^{-9} \text{ s}^{-1}$), we may roughly conclude that an thermal equilibrium for the ground rotational states of C₂H₆ can be achieved from the nucleus up to the contact surface of Hale-Bopp. This rough consideration supports a common idea that cometary molecules within the contact surface is in LTE.

Next we consider vibrational excitation of the v_7 band by electron collisions near the contact surface. To our knowledge, the vibrational excitation rates of the infrared bands of C₂H₆ by collisions with electrons are not available in the literature. With the absence of the rates, we refer to the excitation rates of the infrared bands of CO2 (Takekawa and Itikawa, 1998), H₂O (Nishimura and Itikawa, 1995), and H₂S (Nishimura and Itikawa, 1996), which were experimentally and/or theoretically obtained using low-energy electrons. In the above references, the total excitation crosssections of the infrared bands of the above molecules are found to be less than or equal to 10^{-16} cm² for the electron energy range of 0.5 \sim 1.0 ev, which is also for the $10^5 \sim 5 \times 10^5$ km range of comet P/Halley observed by Vega 1 and 2 (Pedersen et al., 1987). Within the contact surface (<24,000 km), the electron energy rapidly decreases (Cravens, 1989), and therefore the cross-sections will also rapidly decrease accordingly, although the electron density may increase near the contact surface (Balsiger et al., 1986). For comet P/Halley, the electron density near the contact surface was $\sim 5 \times 10^4$ cm⁻³ assuming overall charge neutrality

in the coma. It is not clear that the electron density near the contact surface of Hale-Bopp is 10 times of that of comet P/Halley, but with the absence of the electron density data, here we assume an electron density of 5×10^4 cm⁻³ at the contact surface. Using the cross-section <10-16 cm², the electron energy range of $0.5 \sim 1.0$ ev, and an electron density of $\sim 5 \times 10^5$ cm⁻³, we obtained an excitation rate of $<3 \times 10^{-3}$ s⁻¹ for the ν_7 band. Since the fluorescence excitation rate of the ν_7 band is 6.8×10^{-4} s⁻¹, the vibrational excitation rates of the v_7 band by electron collisions may be significant near the contact surface. Since we do not know the electron densities and cross-sections, we did not attempt to calculate detailed effects in this paper. However, this negligence does not significantly affect the analysis of the observed data, because the spectrometer aimed the center of nucleus with a $1,100 \times 33,000$ km aperture, where most of the C_2H_6 molecules are in LTE.

The collisional deexcitation rates of the vibrational bands by H₂O collisions might be significant near the nucleus of Hale-Bopp, where H_2O density is high. If the deexcitation rates are greater than the Einstein A coefficient of the v_7 band, then radiationless deexcitations from the upper state should be significant. According to experimental results of Holmes et al. (1964), $C_2H_6 \leftrightarrow C_2H_6$ vibrational relaxation rates have two modes, 3.3×10^{-12} cm³ s⁻¹ and 5.3×10^{-11} cm³ s⁻¹ measured at 303 K. We extrapolated the dominant rate (the latter rate) to 130 K assuming the rate to be proportional to $T^{0.5}$, and the result is 3.5×10^{-11} cm³ s⁻¹ at 130 K. Experimental $C_2H_6 \leftrightarrow H_2O$ vibrational relaxation rates are not available in literature to our knowledge. We calculated vibrational deactivation rates of the v_7 band of C_2H_6 by H_2O collisions using a semi-quantum mechanical formulae (so called SSH method) presented by Schwartz Slawsky, and Herzfeld (1952). The $C_2H_6 \leftrightarrow H_2O$ vibration-translation energy transfer rate is found to be almost negligible compared with the above $C_2H_6 \leftrightarrow C_2H_6$ vibrational relaxation rates. According to Schwartz et al., the SSH calculations may give rise factors of 10-30 uncertainties. At the surface of Hale-Bopp, the vibrational relaxation rates using the Holmes et *al.*'s value is 350 s⁻¹; and at the 1500 km from the nucleus the vibrational relaxation rate is $6.9 \times 10^{-3} \text{ s}^{-1}$. The Einstein A ($v = 1 \rightarrow 0$) coefficient of the v_7 band is about 48 s^{-1} . Therefore, there should be significant radiationless vibrational deexcitation very close to the nucleus, but immediately off from the nucleus this effect decreases rapidly. The satisfactory fit in Fig. 5 indicates that the radiationless vibrational deactivation is not apparent within the 1000×2000 km aperture. The satisfactory fit also suggests that an optically thin model for the ${}^{R}Q_{0}$ sub-branch, which we assume throughout this paper, should be appropriate. Pure-rotational transitions due to electron collisions can be ignored because C_2H_6 has no permanent electric dipole moment, as discussed in the main text, and will not be discussed here again.

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