VIBRATIONAL ENERGY TRANSFER BETWEEN HF AND HCN MOLECULES: EXPER--ETC(U)

JUL 78 C WITTIG

N00014-75-C-0567

UNCLASSIFIED


58. J. C. Stephenson, J. Finzi, and C. B. Moore,


73. A. Messiah, Quantum Mechanics. Amsterdam: North-Holland Publishing Co., 1958, Chapters XVII and XIX.


34-43, 1936.

81. See 7.5 (a) of ref. 3.


87. D. Rapp and T. Kassal, "The theory of vibrational


96. J. Finzi, J. H. S. Wang, and F. N. Mastrup, "Transition moments and integrated intensities of HCN(\nu_1+\nu_3) and DCN(\nu_1+\nu_3) combination bands," preprint.


APPENDIX: TRANSITION MOMENTS

Although the relation between the integrated absorption intensity and the transition rate is known for a long time, it has produced confusion among the workers in this laboratory. The relationship is derived below in a simple way and used to calculate the radiative lifetimes and the transition moments of HF and HCN.

Consider a train of light beam with spectral intensity \( I_\nu \) and spatial width \( \Delta l \). When it propagates a distance \( \delta x \) through an absorbing medium, the intensity is attenuated by \( \delta I_\nu \) according to Beer's law

\[
-\delta I_\nu = N_\nu I_\nu \delta x, \quad \text{(A1)}
\]

where \( N \) and \( \alpha_\nu \) are the density and the absorption coefficient of the medium at frequency \( \nu \). The energy absorbed by the medium is determined by the overall transition coefficient of an absorption band. When the absorption band has a narrow spectral width, one has

\[
(h\nu)(B_\nu)(\Delta l/c)(N\delta x) = -\int \delta p_\nu \Delta l d\nu \quad \text{(A2)}
\]
where

\[ \rho_v = I_v/c. \]

By combining (A1) and (A2) one gets

\[ B = \frac{c}{\hbar v} N \int \alpha_v d\nu. \]

The spontaneous emission rate \( A \) can be obtained using the Einstein relation

\[ A = \frac{8\pi \nu^3}{c} B. \]

Finally one has

\[ A = \frac{8\pi \nu^2}{c^2} \frac{1}{N} \int \alpha_v d\nu. \] (A3)

The transition rates due to the dipole and the quadrupole moments can be obtained from Blatt and Weisskopf [99]. For the dipole transition

\[ A = \frac{64\pi^4 \nu^3}{3hc^3} |\tilde{\mu}|^2. \] (A4)

For the quadrupole transition

\[ A = \frac{32\pi^6 \nu^5}{45hc^5} \text{Tr}(Q^* Q). \] (A5)
where

\[ Q_{ij} = \int (3x_i x_j - r^2 \delta_{ij}) \rho(r) d^3x. \]

The quadrupole moment \( Q_2 \) defined by (5.2.2) for an axially symmetric charge distribution is related to \( Q_{ij} \) by

\[ Q_2^2 = \frac{1}{6} \text{Tr}(Q^* \cdot Q). \]

The radiative lifetimes and the dipole transition moments of HF and HCN are calculated using the integrated absorption-intensity measurements [68, 69, 96]. The 2-fold degeneracy of the bending mode of HCN is taken into account. The dipole transition moments are listed in Table 3.

The radiative lifetimes are

- \( \text{HF}(v=1) \) 5.3 msec,
- \( \text{HCN}(0001) \) 13.4 msec.

If the \((v_2 + v_3)\) transition of HCN is caused by the quadrupole moment, then one gets

\[ Q_2^2 = 1.07 \times 10^{-48} \]

which is obviously too big compared to the one obtained from the V-V rate, \( 1.61 \times 10^{-53} \).