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VIBRATIONAL ENERGY TRANSFER BETWEEN HF AND HCN MOLECULES: EXPER--ETC(U)
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Phys., vol. 44, pp. 548-555, 1966.

51. J. F. Bott and N. Cohen, "Temperature dependence of V-V and V-R,T energy transfer measurements in mixtures containing HF," *J. Chem. Phys.*, vol. 59, pp. 4539-4549, 1973.

52. J. F. Bott, "Vibrational relaxation of HF (V=1, 2, and 3) in H_2, N_2, and CO_2," *J. Chem. Phys.*, vol. 65, pp. 4239-4245, 1976.

53. H. L. Chen and C. B. Moore, "Vibration $\rightarrow$ vibration energy transfer in hydrogen chloride mixtures," *J. Chem. Phys.*, vol. 54, pp. 4080-4084, 1971.

54. H. L. Chen, "Vibration-to-vibration energy transfer in hydrogen bromide mixtures," *J. Chem. Phys.*, vol. 55, pp. 5557-5560, 1971.

55. J. L. Ahl and T. A. Cool, "Vibrational relaxation in the HF-HCl, HF-HBr, HF-HI, and HF-DF systems," *J. Chem. Phys.*, vol. 58, pp. 5540-5548, 1973.

56. C. B. Moore, R. E. Wood, B. L. Hu, and J. T. Yardley, "Vibrational energy transfer in CO_2 laser," *J. Chem. Phys.*, vol. 46, pp. 4222-4231, 1967.

57. H. L. Chen, J. C. Stephenson, and C. B. Moore, "Laser-excited vibrational fluorescence of HCl and HCl-CO_2 laser," *Chem. Phys. Lett.*, vol. 2, pp. 593-596, 1968.

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

"Vibration → vibration energy transfer in CO_2-hydrogen halide mixtures," J. Chem. Phys., vol. 56, pp. 5214-5221, 1972.

59. See a review paper; T. A. Cool, "The transfer chemical laser: a review of recent research," IEEE J. Quantum Electron., vol. JQE-1, pp. 72-83, 1973, and references cited therein.

60. L. M. Peterson, G. H. Lindquist, and C. B. Arnold, "Rotation relaxation measurements of laser-excited hydrogen fluoride," J. Chem. Phys., vol. 61, pp. 3480-3482, 1974.

61. J. J. Hinchen and R. H. Hobbs, "Rotational relaxation studies of HF using i.r. double resonance," J. Chem. Phys., vol. 65, pp. 2732-2739, 1976.

62. P. R. Bevington, Data reduction and error analysis for the physical sciences. New york: McGraw-Hill, 1969.

63. S. W. Provencher, "An eigenfunction expansion method for the analysis of exponential decay curves," J. Chem. Phys., vol. 64, pp. 2772-2777, 1976.

64. J. A. McGarvey, Jr., N. E. Friedman, and T. A. Cool, "Vibrational energy transfer in HF-HCN, DF-HCN, and H_2-HCN mixtures," J. Chem. Phys., vol. 66, pp. 3189-3196, 1977.

65. A. Hariri, Ph. D. Thesis, University of Southern California, 1977.

66. D. R. Siebert and G. W. Flynn, "Mode to mode energy transfer in OCS directly pumped by a CO_2 laser," J. Chem. Phys., vol. 64, pp. 4973-4983, 1976.

67. F. J. Zeleznik and R. A. Svehla, "Rotational relaxation in polar gases. II," J. Chem. Phys., vol. 53, pp. 632-646, 1970.

68. G. E. Hyde and D. F. Hornig, "The measurement of bond moments and derivatives in HCN and DCN from infrared intensities," J. Chem. Phys., vol. 20, pp. 647-652, 1952.

69. R. J. Lovell and W. F. Herget, "Lorentz parameters and vibration-rotation interaction constants for the fundamental band of HF," J. Opt. Soc. Am., vol. 52, pp. 1374-1376, 1962.

70. H. D. Mettee, "Vapor-phase dissociation energy of $(HCN)_2$," J. Phys. Chem., vol. 77, pp 1762-1764, 1973.

71. R. K. Thomas, "Hydrogen bonding in the gas phase: the infrared spectra of complexes of hydrogen fluoride with hydrogen cyanide and methyl cyanide," Proc. Roy. Soc. London, vol. A325, pp. 133-149, 1971.

72. H. K. Shin, "Deexcitation of molecular vibration on collision: vibration-to-rotation energy transfer in hydrogen halides," J. Phys. Chem., vol. 75, pp. 1079-1090, 1971; "Vibration-to-rotation energy transfer in hydrogen fluoride: Effects of the dipole-dipole and

hydrogen-bond interactions," *J. Chem. Phys.*, vol. 59, pp. 879-884, 1973.

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

74. C. Zener, "Interchange of translational, rotational and vibrational energy in molecular collisions," *Phys. Rev.*, vol. 37, pp. 556-569, 1931.

75. J. M. Jackson and N. F. Mott, "Energy exchange between inert gas atoms and a solid surface," *Proc. Roy. Soc. London*, vol. A137, pp. 703-717, 1932.

76. N. F. Mott and H. S. W. Massey, *Theory of atomic collision*. New York: Oxford University Press, 1965. 3rd ed.

77. K. Takayanagi, "On the inelastic collision between molecules, I," *Prog. Theoret. Phys.*, vol. 8, pp. 111-119, 1952.

78. R. N. Schwartz, Z. I. Slawsky, and K. F. Herzfeld, "Calculation of vibrational relaxation times in gases," *J. Chem. Phys.*, vol. 20, pp. 1591-1599, 1952.

79. R. N. Schwartz and K. F. Herzfeld, "Vibrational relaxation times in gases (three-dimensional treatment)," *J. Chem. Phys.*, vol. 22, pp. 767-773, 1954.

80. L. Landau and E. Teller, "Zur Theorie der Schalldispersion," *Phys. Z. Sowietunion*, vol. 10, pp.

34-43, 1936.

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

82. K. Takayanagi, "On the Inelastic collision between molecules, II. Rotational transition of H_2-molecule in collision with another H_2-molecule," Prog. Theoret. Phys., vol. 8, pp. 497-508, 1952.

83. D. Rapp and T. E. Sharp, "Vibrational energy transfer in molecular collisions involving large transition probabilities," J. Chem. Phys., vol. 38, pp. 2641-2648, 1963.

84. D. Rapp and P. Englander-Golden, "Resonant and near-resonant vibrational-vibrational energy transfer between molecules in collisions," J. Chem. Phys., vol. 40, pp. 573-575, 1964.

85. R. Marriott, "Molecular collision cross sections and vibrational relaxation in carbon monoxide," Proc. Phys. Soc., vol. A83, pp. 159-169, 1964; "Molecular collision cross sections and vibrational relaxation in carbon dioxide," Proc. Phys. Soc., vol. A84, pp. 877-888, 1964.

86. D. Secrest and R. B. Johnson, "Exact quantum-mechanical calculation of a collinear collision of a particle with a harmonic oscillator," J. Chem. Phys., vol. 45, pp. 4556-4570, 1966.

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

energy transfer between simple molecules in nonreactive collisions," Chem. Rev., vol.69, pp. 61-102, 1969.

88. B. H. Mahan, "Resonant transfer of vibrational energy in molecular collisions," J. Chem. Phys., vol. 46, pp. 98-101, 1967.

89. R. D. Sharma and C. A. Brau, (a) "Near-resonant vibrational energy transfer in N_2-CO_2 mixtures," Phys. Rev. Lett., vol. 19, pp. 1273-1275, 1967; (b) "Energy transfer in near-resonant molecular collisions due to long-range forces with application to transfer of vibrational energy from ν_3 mode of CO_2 to N_2," J. Chem. Phys., vol. 50, pp. 924-930, 1969.

90. B. C. Carlson and G. S. Rushbrooke, "On the expansion of a Coulomb potential in spherical harmonics," Proc. Cambridge Phil. Soc., vol. 46, pp. 626-633, 1950; C. G. Gray, "On the theory of multipole interactions," Can. J. Phys., vol. 46, pp. 135-139, 1968.

91. P. W. Anderson, "Pressure broadening in the microwave and infra-red regions," Phys. Rev., vol. 76, pp. 647-661, 1949.

92. R. D. Sharma and R. R. Hart, "Comparison of classical, distorted wave, and straight path methods of evaluating the integrals over the intermolecular trajectory during molecular collisions," J. Chem.

Phys., vol. 63, pp. 5383-5389, 1975.

93. C. G. Gray and J. van Kranendonk, "Calculation of the pressure broadening of rotational Raman lines due to multipolar and dispersion interaction," Can. J. Phys., vol. 44, pp. 2411-2430, 1966.

94. W. G. Tam, "Vibrational energy transfer probabilities due to Coulomb interaction," Can. J. Phys., vol. 50, pp. 2691-2697, 1972; "Long range force vibrational energy transfer," Chem. Phys. Lett., vol. 15, pp. 113-115, 1972.

95. M. Abramowitz and I. A. Stegun, Handbook of mathematical functions. New York: Dover Publications, Inc., 1965, pp. 1001-1003.

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.

97. M. M. Shapiro and H. P. Gush, "The collision-induced fundamental and first overtone bands of oxygen and nitrogen," Can. J. Phys., vol. 44, pp. 949-963, 1966.

98. T. A. Dillon and J. C. Stephenson, "Multiquantum vibrational-energy exchange," Phys. Rev., vol. A6, pp. 1460-1468, 1972; "Calculation of vibrational and rotational energy transfer between HF, DF, HCl, and CO_2," J. Chem. Phys., vol. 58, pp. 2056-2064, 1973.

99. J. M. Blatt and V. F. Weisskopf, Theoretical nuclear physics. New York: John Wiley & Sons, 1952, Chapter XII and Appendix B.

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_ν and spatial width $\Delta\ell$. When it propagates a distance δx through an absorbing medium, the intensity is attenuated by δI_ν according to Beer's law

$$-\delta I_\nu = N\alpha_\nu I_\nu \delta x, \qquad \text{(A1)}$$

where N and α_ν are the density and the absorption coefficient of the medium at frequency ν. 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

$$(h\nu)(B\rho_\nu)(\Delta\ell/c)(N\delta x) = -\int \delta\rho_\nu \Delta\ell d\nu \qquad \text{(A2)}$$

where

$$\rho_\nu = I_\nu/c.$$

By combining (A1) and (A2) one gets

$$B = \frac{c}{h\nu}\frac{1}{N}\int\alpha_\nu d\nu.$$

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

$$A = \frac{8\pi h\nu^3}{c^3} B.$$

Finally one has

$$A = \frac{8\pi\nu^2}{c^2}\frac{1}{N}\int\alpha_\nu d\nu. \qquad \text{(A3)}$$

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

$$A = \frac{64\pi^4\nu^3}{3hc^3}|\vec{\mu}|^2. \qquad \text{(A4)}$$

For the quadrupole transition

$$A = \frac{32\pi^6\nu^5}{45hc^5}\,\mathrm{Tr}(Q^*\cdot Q), \qquad \text{(A5)}$$

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

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

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

HF(v=1) 5.3 msec,

HCN(00^01) 13.4 msec.

If the $(\nu_2+\nu_3)$ transition of HCN is caused by the quadrupole moment, then one gets

$$Q_2{}^2 = 1.07X10^{-48}$$

which is obviously too big compared to the one obtained from the V-V rate, $1.61X10^{-53}$.