

Calculation of Raman intensities for the torsional vibrations of methylcyclopropane and propylene oxide

David F. Bocian, G. Alan Schick, J. Kathleen Hurd, and Robert R. Birge

Citation: *The Journal of Chemical Physics* **76**, 6454 (1982); doi: 10.1063/1.443010

View online: <http://dx.doi.org/10.1063/1.443010>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/76/12?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Selective calculation of high-intensity vibrations in molecular resonance Raman spectra](#)

J. Chem. Phys. **129**, 204103 (2008); 10.1063/1.3013351

[Calculation of Raman intensities for the torsional vibrations of ethyl halides](#)

J. Chem. Phys. **76**, 4828 (1982); 10.1063/1.442801

[Calculation of Raman intensities for the ringpuckering vibrations of trimethylene oxide and cyclobutane. The importance of electrical anharmonicity](#)

J. Chem. Phys. **74**, 3660 (1981); 10.1063/1.441592

[Raman spectra and internal rotation of methylcyclopropane and its analogs](#)

J. Chem. Phys. **62**, 303 (1975); 10.1063/1.430228

[Calculation of the Infrared Intensity Produced in the Torsional Vibration of Ethane by Coriolis Interaction](#)

J. Chem. Phys. **48**, 1393 (1968); 10.1063/1.1668806



of the sample to ~ 30 K (compare c to b in Fig. 1) causes the disappearance of $(\text{HO}_2)_2$ and the formation of H_2O_2 , presumably by Reaction (1). The possibility of an H atom tunneling through a low barrier height due to an $\text{O}-\text{H}\cdots\text{O}$ bond may be responsible for such a low temperature thermal reaction. We hope our report serves to stimulate further studies on electronic structure, other molecular properties, and reactivities of this interesting chemical species.¹⁸

This report is based upon the research supported in part by the National Science Foundation Grant CHE-79-25451 for spectroscopic studies and the Department of Energy (Office of Basic Energy Sciences) Contract DE-AT-03-76-ER-70217 for photolysis studies.

- ¹(a) P. A. Giguère, J. Phys. Chem. **85**, 3733 (1981); (b) J. L. Arnau and P. A. Giguère, J. Chem. Phys. **60**, 270 (1974); (c) see P. A. Giguère, Chemistry **48**, No. 6, 20 (1976) for a historical review; (d) P. A. Giguère and K. Herman, Can. J. Chem. **48**, 3473 (1970); (e) J. L. Arnau and P. A. Giguère, *ibid.* **53**, 2490 (1975).
- ²(a) R. A. Cox and J. P. Burrows, J. Phys. Chem. **83**, 2560 (1979); and references therein; (b) B. A. Thrush, Acc. Chem. Res. **14**, 116 (1981).
- ³H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, Chem. Phys. Lett. **73**, 43 (1980).
- ⁴M. Diem and E. K. C. Lee, Chem. Phys. **41**, 373 (1979).
- ⁵M. Diem, B. G. MacDonald, and E. K. C. Lee, J. Phys. Chem. **85**, 2227 (1981).
- ⁶J. R. Sodeau and E. K. C. Lee, J. Phys. Chem. **84**, 3358 (1980).
- ⁷H. Dubost, Chem. Phys. **12**, 139 (1976).
- ⁸(a) M. E. Jacox and D. E. Milligan, J. Mol. Spectrosc. **42**, 495 (1972); (b) D. W. Smith and L. Andrews, J. Chem. Phys. **60**, 81 (1974).
- ⁹See L. Fredin, B. Nelander, and G. Ribbegaard, J. Chem. Phys. **66**, 4065, 4073 (1977).
- ¹⁰J. A. Lannon, F. D. Verderame, and R. W. Anderson, Jr., J. Chem. Phys. **54**, 2212 (1971).
- ¹¹(a) G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (Freeman, San Francisco, 1960), p. 210; (b) S. N. Vinogradov and R. H. Linnell, *Hydrogen Bonding* (Van Nostrand, New York, 1971); (c) E. J. Hamilton, Jr., and C. A. Naleway, J. Phys. Chem. **80**, 2037 (1976); (d) L. C. Allen, J. Am. Chem. Soc. **97**, 6921 (1975); (e) H. Umeyama and K. Morokuma, *ibid.* **99**, 1316 (1977).
- ¹²W. Hagen and A. G. G. M. Tielens, J. Chem. Phys. **75**, 4198 (1981).
- ¹³P. A. Giguère and T. K. K. Srinivasan, Chem. Phys. Lett. **33**, 479 (1975).
- ¹⁴C. J. Howard, J. Am. Chem. Soc. **102**, 6937 (1980).
- ¹⁵The current best estimate of $\Delta H_f^\circ(298) = -3.2$ kcal/mol for H_2O_2 (open chain) is obtained from the group additivity rule (D. M. Golden, private communication, based on a recent compilation by A. C. Baldwin), and an estimate of 5.5 kcal/mol was given earlier by S. W. Benson, *Thermochemical Kinetics* (Wiley, New York, 1976), p. 294.
- ¹⁶Since the $\text{O}-\text{H}\cdots\text{O}$ bonding in the cyclic $(\text{HO}_2)_2$ involves an unpaired electron, it may be somewhat stronger than ~ 7 kcal/mol given for the linear $\text{O}-\text{H}\cdots\text{O}$ bond (Ref. 11), even though it is not linear. Electronic stabilization energies of 9.1 and 12.0 kcal/mol have been calculated for $\text{HO}_2\cdots\text{H}_2\text{O}$ and $\text{HO}_2\cdots\text{NH}_3$ complexes, respectively [Ref. 11(a)].
- ¹⁷For example, the observed $\text{H}_2\text{O}_2\cdots\text{X}$ complex peaks at 3541 (ν_5) and 1296 cm^{-1} (ν_6) in O_2 are shifted -56 and $+25$ cm^{-1} , respectively, from the monomer frequencies reported at 3597 (ν_5) and 1271 cm^{-1} (ν_6) in N_2 (Ref. 10). Note that the most of CO molecules are complexed to $(\text{HO}_2)_2$ at 2160–2163 cm^{-1} in the 10 min photolysis sample in Fig. 1(a).
- ¹⁸H. E. Hunziker (private communication) reported the disappearance of the $\text{O}-\text{H}$ overtone absorption at 1.5 μm in the $\text{HO}_2\cdots\text{NH}_3$ complex due to hydrogen bonding at the 14th Informal Photochemistry Conference, Newport Beach, California, March 30–April 4, 1980.

Calculation of Raman intensities for the torsional vibrations of methylcyclopropane and propylene oxide

David F. Bocian, G. Alan Schick, J. Kathleen Hurd, and Robert R. Birge

Department of Chemistry, University of California, Riverside, California 92521
(Received 8 February 1982; accepted 3 March 1982)

We recently reported the calculation of molecular polarizability expansions and Raman intensities for the puckering vibrations of a number of small ring molecules¹ and for the torsional vibrations of several ethyl halides.² The calculations predict unusually large electrically anharmonic terms in the expansions of the molecular polarizability tensor elements in the vibrational coordinate for both types of large-amplitude motion. The large electrical anharmonicity results in intense calculated $\Delta v=2$ overtones, in agreement with experiment.^{3–16} The calculations also predict the electrical anharmonicity contributes substantially to the intensity of the $\Delta v=1$ transitions of both the puckering

motions of certain of the ring molecules^{1(b)} and the torsional oscillations of the ethyl halides.² In the case of the ethyl halides, however, the $\Delta v=1$ torsional transitions are not observed, in part because these transitions are expected to have broad band contours but also because the region of the spectrum in which they are expected is obscured by other low-frequency vibrations.^{15,16} Consequently, the accuracy of the calculated intensities of the $\Delta v=1$ torsional transitions cannot be checked. Two molecules for which both the $\Delta v=1$ ¹⁷ and $\Delta v=2$ ¹⁸ torsional transitions are observed are methylcyclopropane and propylene oxide. In this note we report the calculation of Raman intensities for the methyl

TABLE I. Observed and calculated Raman intensities for methylcyclopropane and propylene oxide.

Molecule	Transition	Frequency (cm ⁻¹) ^a	Relative intensity		
			Observed ^a	Calculation I ^b	Calculation II ^c
Methylcyclopropane	0-1	224	(1.0) ^d	(1.0)	0.033
	1-2	206	0.93 ^d	0.50	0.023
	2-3	189	0.79 ^d	0.27	0.014
	0-2	413	... ^e	0.027	4.1 × 10 ⁻⁴
	1-3	384	... ^e	0.028	4.8 × 10 ⁻⁴
	2-4	341	... ^e	0.021	4.1 × 10 ⁻⁴
Propylene oxide	0-1	200	(1.0)	(1.0)	0.12
	1-2	186	0.64	0.72	0.095
	2-3	169	0.23	0.26	0.062
	0-2	388	... ^e	0.026	1.7 × 10 ⁻³
	1-3	357	... ^e	0.028	2.2 × 10 ⁻³

^aThe frequencies and observed intensities of the $\Delta v = 1$ and $\Delta v = 2$ transitions were taken from Refs. 17 and 18, respectively. The intensities were estimated from the peak heights in Fig. 1 of the two references.

^bCalculated using the complete polarizability expansions (see Ref. 2).

^cCalculated neglecting electrical anharmonicity by including only the first-order terms in the polarizability expansions (see Ref. 2).

^dThese transitions have extremely broad band contours so the intensities cannot be determined accurately.

^eThe $\Delta v = 2$ transitions of both molecules appear as weak shoulders on the much more intense in- and out-of-plane bending modes of the methyl group (see Fig. 1 of Ref. 18), so the intensities cannot be measured accurately. The $\Delta v = 2$ transitions, observed for the respective molecules do, however, appear to be approximately equal in intensity, as is predicted by the calculations.

torsional transitions of these molecules.

The method for calculating the Raman intensities for the torsional vibrations of methylcyclopropane and propylene oxide was identical to that used for the ethyl halides.² First, the molecular polarizability tensor was calculated as a function of the torsional angle using an anisotropic atom-point dipole interaction model.¹⁹ The parameters used in the polarizability model for the carbon, hydrogen and oxygen atoms were taken from Ref. 19. Next, the elements of the molecular polarizability tensor were expanded in trigonometric series by obtaining the Fourier transform of the polarizability calculated as a function of the torsional angle. Finally, the Raman intensities of the torsional transitions were evaluated using the polarizability expansions and Eqs. (1)–(3) of Ref. 2.

The relative Raman intensities calculated for the torsional transitions of methylcyclopropane and propylene oxide are listed along with the observed intensities in Table I. The transitions are given in terms of the high-barrier quantum number v which is appropriate for the lowest torsional levels of the two molecules.^{17,18} The intensities are the total intensities for the transitions between the triply degenerate levels. The calculations predict that the torsional transitions of the two molecules have nearly the same intensity distributions. These intensity distributions are also quite similar to those calculated for the torsional transitions of the ethyl halides.² The observed intensity distribution of the $\Delta v = 1$ transitions of propylene oxide is well reproduced by the calculations. The calculated intensities of the $\Delta v = 1$ transitions of methylcyclopropane do not appear

to be in as good agreement with experiment; however, the observed transitions are extremely broad so the intensities cannot be measured accurately.¹⁷ The calculations predict that the $\Delta v = 2$ torsional overtones of methylcyclopropane and propylene oxide are much weaker than the $\Delta v = 1$ fundamentals. Unfortunately, the $\Delta v = 2$ transitions of both molecules appear as shoulders on the much more intense in- and out-of-plane bending vibrations of the methyl group so the intensities cannot be measured accurately.¹⁸ In Ref. 17, it is stated that the overtone transitions appear to be more intense than the fundamentals. However, some of the observed intensity of the $\Delta v = 2$ transitions may result from intensity borrowing from the intense methyl bending modes, further precluding the accurate comparison of the calculated and observed intensities of the overtones.

Finally, the contribution of electrically anharmonic terms to the Raman intensities can be determined by performing the calculations including only the first-order terms in the polarizability expansions (see Ref. 2). The results of these calculations are given in Table I. Exclusion of the electrically anharmonic terms results in a decrease in the calculated intensities of both the $\Delta v = 1$ and $\Delta v = 2$ transitions by one to two orders of magnitude. In the case of propylene oxide, exclusion of the electrically anharmonic terms results in an intensity distribution of the $\Delta v = 1$ transitions [$I(0-1):I(1-2):I(2-3) = 1.0:0.79:0.52$] which is clearly in much poorer agreement with the experimental distribution [$I(0-1):I(1-2):I(2-3) = 1.0:0.64:0.23$] than that obtained using the complete polarizability expansions [$I(0-1):I(1-2):I(2-3) = 1.0:0.72:0.26$].

This work was supported by the Donors of the Petroleum Research Fund (D.F.B.), administered by the American Chemical Society; Research Corporation (D.F.B.); the National Institutes of Health (R.R.B.); the National Science Foundation (R.R.B.); and the Committee on Research, University of California, Riverside (D.F.B. and R.R. B.).

¹(a) D. F. Bocian, G. A. Schick, and R. R. Birge, *J. Chem. Phys.* **74**, 3660 (1981); (b) **75**, 2626, 3215 (1981).

²D. F. Bocian, G. A. Schick, J. K. Hurd, and R. R. Birge, *J. Chem. Phys.* (in press).

³For a review of gas-phase Raman studies of large-amplitude vibrations see C. J. Wurrey, J. R. Durig, and L. A. Carreira, in *Vibrational Spectra and Structure*, edited by J. R. Durig (Elsevier, New York, 1976), Vol. 5, pp. 121-277.

⁴J. M. R. Stone and I. M. Mills, *Mol. Phys.* **18**, 631 (1970).

⁵F. A. Miller and R. J. Capwell, *Spectrochim. Acta Part A* **27**, 1947 (1971).

⁶(a) W. Kiefer, H. J. Bernstein, M. Danyluk, and H. Wieser, *Chem. Phys. Lett.* **12**, 605 (1972); (b) *J. Mol. Spectrosc.*

43, 393 (1972).

⁷J. R. Durig and L. A. Carreira, *J. Chem. Phys.* **56**, 4966 (1972).

⁸T. H. Chao and J. Laane, *Chem. Phys. Lett.* **14**, 595 (1972).

⁹J. R. Durig, L. A. Carreira, and J. N. Willis, Jr., *J. Chem. Phys.* **57**, 2755 (1972).

¹⁰L. A. Carreira, R. O. Carter, and J. R. Durig, *J. Chem. Phys.* **57**, 3384 (1972).

¹¹J. R. Durig, A. C. Shing, L. A. Carreira, and Y. S. Li, *J. Chem. Phys.* **57**, 4398 (1972).

¹²J. R. Durig, A. C. Shing, and L. A. Carreira, *J. Mol. Struct.* **17**, 423 (1973).

¹³J. R. Durig, R. O. Carter, and L. A. Carreira, *J. Chem. Phys.* **59**, 2249 (1973).

¹⁴J. D. Lewis, T. H. Chao, and J. Laane, *J. Chem. Phys.* **62**, 1932 (1975).

¹⁵J. R. Durig, W. E. Bucy, L. A. Carreira, and C. J. Wurrey, *J. Chem. Phys.* **60**, 1754 (1974).

¹⁶J. R. Durig, W. E. Bucy, and C. J. Wurrey, *J. Chem. Phys.* **60**, 3293 (1974).

¹⁷J. R. Villareal and J. Laane, *J. Chem. Phys.* **62**, 303 (1975).

¹⁸J. R. Durig, A. D. Lopata, and C. J. Wurrey, *J. Raman Spectrosc.* **3**, 345 (1975).

¹⁹R. R. Birge, *J. Chem. Phys.* **72**, 5312 (1980).

ERRATA

Erratum: Elastic constants of nematic and cholesteric liquid crystals and tensor fields [*J. Chem. Phys.* **76**, 616 (1982)]

G. Vertogen, S. D. P. Flapper, and C. Dullemond

Institute for Theoretical Physics, Catholic University, Toernooiveld, 6525 Ed Nijmegen, The Netherlands

Throughout the paper, ρ should be replaced by ρ^2 , whereas Eq. (3.10) should read

$$\frac{2\pi}{3} \rho^2 \int A(\epsilon) \epsilon^3 d\epsilon [\mathbf{n}(\mathbf{r}) \cdot \mathbf{V} \wedge \mathbf{n}(\mathbf{r})] . \quad (3.10)$$

Erratum: A calorimeter for heat capacity measurements of high precision from 1.4 to 100 K. The heat capacity of hexammine cobalt(111) chloride from 2.1 to 309 K [*J. Chem. Phys.* **75**, 5464 (1981)]

P. R. Clayton, L. A. K. Staveley, and R. D. Weir

The Inorganic Chemistry Laboratory, The University of Oxford, South Parks Road, Oxford OX1 3QR, England

The barrier height of the Schottky anomaly, reported in the last line of the abstract, should read 4.7 in lieu of 3.9 kJ mol⁻¹.