# Relation between Shapes of Infrared Absorption Bands and Thermodynamic Properties of Condensed Systems

**2 AUTHORS:**

Harry Friedmann
Bar Ilan University

**146** PUBLICATIONS   **2,288** CITATIONS

Sol Kimel
Technion - Israel Institute of Technology

**139** PUBLICATIONS   **2,353** CITATIONS

H. Friedmann and S. Kimel
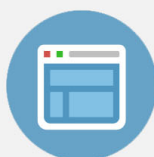
trigonal axis) between 300° and 1000°K are shown in Table I. While $\chi_{||}$ follows the Curie dependence $C/(T+\theta)$ over the entire temperature interval, $\chi_\perp$ does show appreciable deviation above 500°K.

The magnetic susceptibilities were calculated by the general expression Eq. (22) of Ref. 5. They depend on such crystal-field parameters as the spin–orbit coupling constant $\lambda$ and the two trigonal-field parameters $\gamma$ and $\tau$ which were defined in Ref. 5. Since $\Delta_T$ can be expressed as a linear combination of $\gamma$ and $\tau$, we can use $\Delta_T$ and $\tau$ as the two parameters describing the trigonal distortion. When this is done, we found that $\chi_{||}$ and $\chi_\perp$ depend primarily on $\Delta_T$ but are very insensitive to $\tau$ ($\tau$ being the trigonal-field term proportional to $\langle r^2 \rangle$). Furthermore, $\Delta_T$ and $\lambda$ are related to $g_{||}$ which is equal to 1.915 from the ESR spectrum[1]; thus for a given $\Delta_T$ we can calculate $\chi_{||}$ and $\chi_\perp$. It is found that the theo-
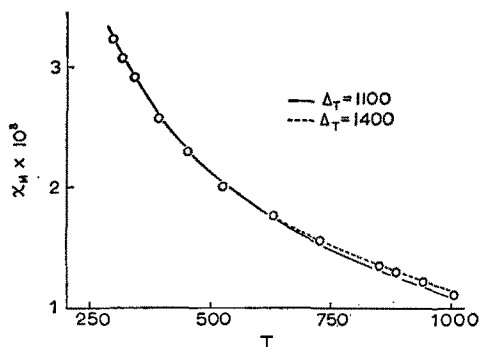


FIG. 1. Magnetic susceptibilities $\chi_\perp$ of $V^{3+}:Al_2O_3$ versus $T$ for the interval 300°–1000°K. The circles are the experimental points. The solid curve represents the theoretical values calculated by using $\Delta_T = 1100$ cm$^{-1}$ and the dotted curve for $\Delta_T = 1400$ cm$^{-1}$.

retical susceptibilities can be fitted to the experimental values by choosing $\Delta_T = 1200 \pm 200$ cm$^{-1}$ and $\lambda = 95 \pm 5$ cm$^{-1}$. Figure 1 shows the theoretical and experimental values of $\chi_\perp$. Good agreement was also obtained for $\chi_{||}$. Here the temperature variation is of the Curie type over the entire range of 300° to 1000°K, and hence will not be displayed graphically. In the above analysis we have chosen the orbital reduction factor[8] $k$ as unity. One can justify this from the ionic nature of the $Al_2O_3$ crystal which is reflected by the rather small reduction of $\lambda$ from its free-ion value. Furthermore, like the case of $Ni^{2+}:ZnO$ and $Ni^{2+}:CdS$,[9] the inclusion of $k$ in the theoretical equations of $\chi$ has little effect on the shape of the curve of $\chi$ versus $T$ and will not cause any change in the crystal-field parameters. The value of $\Delta_T$ obtained from this experiment agrees well with that determined from the magnetic data at lower temperatures and also with the results of optical spectra.

[1] C. M. Zverev and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. 34, 1033 (1958); 38, 449 (1960); 40, 1016 (1961) [English transls.: Soviet Phys.—JETP 7, 707 (1958); 11, 330 (1960); 13, 714 (1961)].
[2] S. Foner and W. Low, Phys. Rev. 120, 1585 (1960).
[3] D. S. McClure, J. Chem. Phys. 36, 2757 (1962).
[4] M. H. L. Pryce and W. A. Runciman, Discussions Faraday Soc. 26, 35 (1958).
[5] W. H. Brumage, C. R. Quade, and C. C. Lin, Phys. Rev. 131, 949 (1963).
[6] C. R. Quade, W. H. Brumage, and C. C. Lin, J. Chem. Phys. 37, 1368 (1962).
[7] M. Garber, W. G. Henry, and H. G. Hoeve, Can. J. Phys. 38, 1595 (1960).
[8] W. Low, Solid State Phys. Suppl. 2, 99, 100 (1960).
[9] W. H. Brumage and C. C. Lin, Phys. Rev. 134, A950 (1964).

# Relation between Shapes of Infrared Absorption Bands and Thermodynamic Properties of Condensed Systems*

H. Friedmann and S. Kimel

*The Weizmann Institute of Science, Rehovoth, Israel*

(Received 20 October 1964)

INFORMATION about intermolecular forces is implicitly contained in optical spectra of condensed phases. However, there have been few cases where it has been found possible to predict thermodynamic properties of interacting systems from spectroscopic observations. The present study concerns a case in which a direct relationship between spectroscopic and thermodynamic properties is established.

Gordon has shown[1,2] that the average angular Laplacian of the intermolecular potential energy, $\langle \nabla_\Omega^2 V \rangle = \langle \partial^2 V/\partial\theta^2 + \cot\theta(\partial V/\partial\theta) + \csc^2\theta(\partial^2 V/\partial\phi^2) \rangle$, can be determined from the third and the fourth moments of the intensity distribution in rotation–vibration bands. The same quantity can also be obtained from data on changes in thermodynamic properties with isotopic substitution.[3]

Values of $\langle \nabla_\Omega^2 V \rangle$ for CO have been determined[2] from the spectra of gaseous, liquid, and solid phases.[4,5] In the present note $\langle \nabla_\Omega^2 V \rangle$ is determined using vapor-pressure ratios of isotopic carbon monoxides. These are anomalous[6] and can be accounted for[3] by assuming that (a) the intermolecular potential energy depends on $\mathbf{r}^N$, the positions of the *centers of interaction* of the $N$ molecules of the system; and (b) at temperatures not too far below the melting point, quantum effects are small so that it is sufficient to retain terms up to order $h^2$ in the expansion of the partition function in powers of Planck's constant.

The center of interaction is fixed with respect to the charge distribution in the molecule and consequently the potential energy, expressed in the form $V(\mathbf{r}^N)$, is isotope invariant. Furthermore, since the center of interaction does not coincide with the center of mass, $V(\mathbf{r}^N)$ is an angle-dependent potential, although of a particularly simple form. One can readily derive the following relation between the average angular and linear Laplacians[7]

$$\langle \nabla_\Omega^2 V(\mathbf{r}^N) \rangle_{\text{cl}} = \tfrac{2}{3}a^2 \langle \nabla^2 V(\mathbf{r}^N) \rangle_{\text{cl}}, \qquad (1)$$

where the symbol $\langle \; \rangle_{\text{cl}}$ denotes an average taken over

TABLE I. Comparison between thermodynamic and spectroscopic average angular Laplacians in condensed carbon monoxide.

| | | Thermodynamic | | Spectroscopic | |
| | | $[\langle \nabla_\Omega^2 (V/kT) \rangle_{cl}]^{\frac{1}{2}}$ | | $[\langle \nabla_\Omega^2 (V/kT) \rangle]^{\frac{1}{2}}$ | $\langle [\nabla_\Omega (V/kT)]^2 \rangle^{\frac{1}{2}}$ |
| | Temperature (°K) | From Eqs. (1) and (2) | | From third moment | From fourth moment |
| $\beta$-solid | 67 | 2.5 | | 5. | 4.0 |
| liquid | 80 | 2.0 | | 5. | 4.4 |

the classical Boltzmann distribution and $a$ is the distance between the center of mass and the center of interaction in a molecule.

The simple form of Eq. (1) only holds if rotation of the molecules about their centers of interaction is unhindered. Otherwise $V$ would also depend *explicitly* on the orientational angles $\Omega^N$ of the molecules. Data on the second virial coefficient of CO seem to indicate,[8] however, that for this molecule noncentral forces can be neglected. Moreover, the high symmetry of the field experienced by a condensed molecule reduces the importance of angular forces.

The average Laplacian can be calculated from the vapor-pressure ratio $p_1/p_2$ of pure isotopes,[3]

$$\langle \nabla^2 V \rangle_{cl} = \frac{24(2\pi kT)^2 \ln(p_1/p_2)}{h^2 [(M_{eff})_1^{-1} - (M_{eff})_2^{-1}]}. \qquad (2)$$

Here $1/M_{eff} = (1/M)(1+2Ma^2/3I)$, where $M$ and $I$ are, respectively, the total mass of a molecule and its moment of inertia. The effective mass $M_{eff}$ depends on the position of the center of interaction. In CO the latter was found to be situated on the internuclear axis at 0.43 A from the carbon nucleus[3] so that, for the isotopes $^{12}C^{16}O$, $^{13}C^{16}O$, and $^{12}C^{18}O$, $a$ takes the values 0.21, 0.19, and 0.24 Å, respectively.

The average Laplacian in Eq. (2) refers to the solid state; a small term containing the corresponding average for the vapor phase[9] has been omitted. To obtain $\langle \nabla_\Omega^2 V \rangle$ for the liquid phase the ratio $p_1/p_2$ in Eq. (2) should be replaced by the isotope-separation factor.[10,11]

In Table I the values for $[\langle \nabla_\Omega^2 (V/kT) \rangle_{cl}]^{\frac{1}{2}}$, obtained by combining Eqs. (1) and (2) and using experimental data on the vapor pressures[6] and the isotope-separation factor,[12] are compared with $[\langle \nabla_\Omega^2 (V/kT) \rangle]^{\frac{1}{2}}$ and with $\langle [\nabla_\Omega (V/kT)]^2 \rangle^{\frac{1}{2}}$ determined by Gordon[2] from the third and fourth moments, respectively. It should be noted [Assumption (b) above] that at these temperatures quantum-mechanical and classical averages are nearly equal, so that $\langle \nabla_\Omega^2 V \rangle \approx \langle \nabla_\Omega^2 V \rangle_{cl} = \langle (\nabla_\Omega V)^2 \rangle_{cl}/kT \approx \langle (\nabla_\Omega V)^2 \rangle/kT$.

The spectroscopic and thermodynamic values for $\langle \nabla_\Omega^2 V \rangle^{\frac{1}{2}}$ in CO are seen to be in agreement within a factor of 2 or so. Better quantitative agreement might be obtained by taking into account changes in intermolecular forces with isotopic substitution,[13] which have been neglected in the derivation of Eq. (2).

The spectroscopic result may also be in error since uncertainties of photometry of infrared bands, in any case large, are of particular significance when calculating higher moments.

It is evident nevertheless that Gordon's moment analysis of band spectra gives an estimate for the average angular Laplacian[14] and should thus become an important tool in the theory of vapor pressures of isotopes.[15] The method could also be applied to the study of molecular reorientation processes.[16] By using the Wigner expansion of the partition function of nonlinear molecules[17] the method could be extended, thus providing a direct link between spectroscopic and thermodynamic properties of condensed systems of polyatomic molecules.

The authors are indebted to Professor J. H. Jaffe for stimulating discussions.

[1] R. G. Gordon, J. Chem. Phys. 37, 2587 (1962); 38, 1724 (1963); 39, 2788 (1963); 40, 1973 (1964).
[2] R. G. Gordon, J. Chem. Phys. 41, 1819 (1964).
[3] H. Friedmann, Advan. Chem. Phys. 4, 225 (1962).
[4] H. Vu, M. R. Atwood, and B. Vodar, J. Chem. Phys. 38, 2671 (1963).
[5] G. E. Ewing, J. Chem. Phys. 37, 2250 (1962).
[6] T. F. Johns, Proc. Intern. Symp. Isotope Separation, Amsterdam 1957, 74 (1958).
[7] See Ref. 3, Eqs. V-17, 18, and 18a.
[8] E. A. Mason and E. Rice, J. Chem. Phys. 22, 843 (1954).
[9] G. Boato, G. Casanova, and A. Levi, J. Chem. Phys. 37, 201 (1962).
[10] G. Boato, G. Casanova, and M. E. Vallauri, Nuovo Cimento 20, 87 (1961).
[11] J. Bigeleisen, J. Chim. Phys. 60, 35 (1963).
[12] E. Ancona, G. Boato, and G. Casanova, Nuovo Cimento 24, 111 (1962).
[13] These changes of intermolecular forces are due to the fact that the potential-energy operator $V(r^N)$ which governs the rotational and translational motion of the molecules is obtained after integrating over the intramolecular electronic and vibrational coordinates, using the Born–Oppenheimer method. The operator $V(r^N)$ then depends on the electronic and on the vibrational (ground) state of the molecules. Since the vibrational state of a molecule depends on the masses of the constituent atoms, the intermolecular forces for two isotopes are (slightly) different.
[14] This is particularly interesting in cases where Assumption (a) and hence Eq. (1) are not valid so that $\langle \nabla_\Omega^2 V \rangle$ cannot be determined using the thermodynamic procedure presented here.
[15] The spectroscopic determination of $\langle \nabla_\Omega^2 V \rangle$ at various pressures could be useful in the determination of changes of molecular volume with isotopic substitution. [H. Friedmann and W. A. Steele, J. Chem. Phys. 40, 3669 (1964).]
[16] W. A. Steele, J. Chem. Phys. 38, 2404, 2411 (1963).
[17] H. Friedmann, Physica 30, 921 (1964).