

While the spectrum of the orthorhombic crystal is in agreement with group-theoretical predictions,⁴ that of the cubic crystal is at variance, although the very broad and weak absorption may well be a superposition of two broad bands. The disappearance of the sharp spectral features may be attributed to the higher degree of freedom of molecular motions (of rotational or librational character) in the cubic phase, which for the same relative temperature, T/T_{melting} , is more prone to molecular disorder than the orthorhombic phase.

A full report on the lattice spectra of acetylene, ethylene, and ethane, the band positions, widths, and intensities and their temperature dependence will be given elsewhere.

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¹ T. Sugawara and E. Kanda, *Sci. Rept. Res. Inst., Tohoku Univ., Ser. A* **2**, 216 (1950).

² E. Krikorian, Ph.D. thesis, Columbia University, New York, 1957.

³ G. L. Bottger and D. F. Eggers Jr., *J. Chem. Phys.* **40**, 2019 (1964); **44**, 4366 (1966).

⁴ A. Anderson and W. H. Smith, *J. Chem. Phys.* **44**, 4216 (1966).

⁵ W. H. Smith and G. E. Leroi (private communication).

⁶ A. Ron and M. Brith (unpublished results).

⁷ G. M. Arnold and R. Heastie, *Chem. Phys. Letters* **1**, 51 (1967).

⁸ R. V. St. Louis and O. Schnepf, *J. Chem. Phys.* **50**, 5177 (1969).

⁹ C. Postmus, V. A. Maroni, J. R. Ferraro, and S. S. Mitra, *Inorg. Nucl. Chem. Letters* **4**, 269 (1968).

¹⁰ A. Loewenschuss, A. Ron, and O. Schnepf, *J. Chem. Phys.* **49**, 272 (1968).

TABLE I. Comparison of observed and calculated intensities of selected ν'' progressions of the $O_2^+ A \ ^2\Pi_u - X \ ^2\Pi_g$ second negative transition.^a

ν''	λ (Å)	Observed intensity	Calculated intensity		
			Old numbering	New ^{1,2} numbering	New numbering plus one
$\nu' = 6$					
4	2667	10.0	10.0	10.0	2.5
5	2797	<0.9	2.7	0.1	2.7
6	2937	6.8	0.3	4.6	10.0
$\nu' = 7$					
7	3023	10.0	10.0	10.0	1.1
8	3182	<0.7	1.6	0.3	5.7
9	3354	5.7	1.9	9.4	10.0
$\nu' = 10$					
4	2490	<1.4	2.4	1.6	10.0
5	2603	10.0	5.6	10.0	7.2
6	2724	<2.7	10.0	2.5	0.1

^a The wavelength is that of the long-wavelength head and ν'' is the new numbering.

sensitivity can provide evidence in support of the proposed change in numbering.

We are preparing a comprehensive tabulation of diatomic Franck-Condon factors based on RKR potential curves constructed from the best available spectroscopic data.⁵ Using Franck-Condon factors calculated by the above method⁶ we have constructed intensity arrays for the second negative system based upon the "old" numbering, the "new" numbering and the "new" numbering plus one. We have also made relative intensity measurements on this system excited by a 5-kV electron beam. The molecular emission was recorded photoelectrically with a double Ebert monochromator whose transmission had been calibrated using a tungsten-strip lamp. Shown in Table I is a comparison of the above-measured intensities with the calculated intensities for some ν'' progressions selected for their sensitivity to the renumbering. Within a progression all intensities are normalized to 10 for the strongest band.

Examination of Table I shows that in all cases the intensity calculated using the new numbering agrees best with the observed intensities. Both the old numbering and the new numbering plus one are clearly inferior. Although the ν'' progressions in Table I were selected for maximum sensitivity, an analysis of all these ν'' progressions that we observed showed that in every progression the new numbering is better than or at

Notes

Evidence in Support of the Vibrational Renumbering of the $O_2^+ \ ^2\Pi_g$ Ground State

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Recently Asundi¹ has suggested that the vibrational numbering of the ground state of O_2^+ be increased by one unit. Bhale and Ramakoteswara Rao² have presented isotope-shift data for the $O_2^+ A \ ^2\Pi_u - X \ ^2\Pi_g$ second negative system supporting this suggestion. Four years ago a similar situation occurred in the vibrational numbering of the $B \ ^3\Pi_{0,u^+}$ state of I_2 . There it was shown both by isotope-shift data³ and by a comparison of calculated and observed intensities⁴ that the vibrational numbering had to be reduced by one unit. This has prompted us to consider the question of how sensitive the calculated intensities of the O_2^+ second negative system would be to changes in the ground-state vibrational numbering, and whether this

least as good as the old numbering or the new numbering plus one. Furthermore, the conclusions above also apply to the collection of intensity eye estimates tabulated by Wallace.⁷ Based on the foregoing we feel that a comparison of observed and calculated intensities strongly supports the vibrational renumbering of the O_2^+ ground state.

We wish to point out that this renumbering has the following consequences. As noted by Asundi,¹ the ionization potential of O_2 now has the value 12.059 ± 0.001 eV, rather than the previously accepted value of 12.063 ± 0.001 eV. In addition, previous calculations of Franck-Condon factors for the $O_2^+ A^2\Pi_u - X^2\Pi_g$ second negative system⁸⁻¹⁶ as well as the ionizing $O_2 X^2\Sigma_g^- \rightarrow O_2^+ X^2\Pi_g$ transition¹⁶⁻¹⁸ must be re-evaluated. Conclusions based on these previous studies, such as the variation of the electronic transition moment $R_e^2(\bar{r}_{v',v''})$ with internuclear distance,¹⁹ or the oscillator strength deduced from fluorescent intensity measurements²⁰ must be reconsidered. For example, we note that when the intensity data of Robinson and Nicholls¹⁹ is analyzed using the Franck-Condon factors and r centroids based on the new numbering, the variation of $R_e^2(\bar{r}_{v',v''})$ substantially differs in magnitude and form from that previously reported. Finally, we have found that the anomaly in Robertson's data²¹ for the Penning process leading to the second negative system of O_2^+ is reduced, if not eliminated, by the use of Franck-Condon factors based on the new numbering.

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¹ R. K. Asundi, *Current Sci. (India)* **37**, 160 (1968).

² G. L. Bhale and P. Ramakoteswara Rao, *Proc. Indian Acad. Sci.* **A67**, 350 (1968).

³ R. L. Brown and T. C. James, *J. Chem. Phys.* **42**, 33 (1965).

⁴ J. I. Steinfeld, R. N. Zare, L. Jones, M. Lesk, and W. Klemperer, *J. Chem. Phys.* **42**, 25 (1965).

⁵ D. L. Albritton, A. L. Schmeltekopf, and R. N. Zare, *Diatom Franck-Condon Factors* [Harper and Row Publishers, Inc., New York (to be published)].

⁶ R. N. Zare, "Programs for Calculating Relative Intensities in the Vibrational Structure of Electronic Band Systems," Rept. UCRL-10925, Lawrence Radiation Laboratory, Berkeley, Calif. 1963.

⁷ L. Wallace, *Astrophys. J. Suppl.* **7**, 165 (1962).

⁸ M. E. Pillow, *Proc. Phys. Soc. (London)* **A63**, 940 (1950).

⁹ T.-Y. Wu, *Proc. Phys. Soc. (London)* **A65**, 965 (1952).

¹⁰ G. Poots, *Proc. Phys. Soc. (London)* **A66**, 1181 (1953).

¹¹ W. R. Jarman, P. A. Fraser, and R. W. Nicholls, *Astrophys. J.* **118**, 228 (1953); R. W. Nicholls, P. A. Fraser, W. R. Jarman, and R. P. McEachran, *ibid.* **131**, 399 (1960).

¹² N. R. Tawde and M. I. Savadatti, *Proc. Phys. Soc. (London)* **71**, 514 (1958).

¹³ M. Halmann and I. Laulicht, *J. Chem. Phys.* **43**, 438 (1965).

¹⁴ R. W. Nicholls, *Can. J. Phys.* **43**, 1390 (1965).

¹⁵ T. Wentink, Jr., L. Isaacson, and R. J. Spindler, "Research on the Opacity of Low Temperature Air: Oscillator Strengths and Transition Moments of Band Systems of N_2 , O_2 , and NO ," Air Force Weapons Laboratory Rept. AFWL-TR-65-139, December 1965.

¹⁶ M. E. Wacks and M. Krauss, *J. Chem. Phys.* **35**, 1902 (1961); M. E. Wacks, *J. Chem. Phys.* **41**, 930 (1964).

¹⁷ M. Halmann and I. Laulicht, *J. Chem. Phys.* **43**, 1503 (1965).

¹⁸ R. W. Nicholls, *J. Phys. B* **1**, 1192 (1968).

¹⁹ D. Robinson and R. W. Nicholls, *Proc. Phys. Soc. (London)* **71**, 957 (1958).

²⁰ M. Jeunehomme, *J. Chem. Phys.* **44**, 4253 (1966).

²¹ W. W. Robertson, *J. Chem. Phys.* **44**, 2456 (1966).

Value of the Critical Absorption Coefficient in Stimulated Thermal Rayleigh Scattering

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Since it was first theoretically predicted by Herman and Gray,¹ stimulated thermal Rayleigh scattering (STRS) has been observed²⁻⁴ in colored liquids and gases. As more than one nonlinear process is possible in such media, e.g., STRS and stimulated Brillouin scattering, it is necessary that the gain for STRS must be larger than or equal to the gain for competing nonlinear processes before it can be detected. Herman and Gray¹ by comparing the gains per unit length for STRS and stimulated Brillouin scattering have deduced that the absorption α of the medium must exceed a critical absorption, α_{cr} , before STRS may be observable, viz.,

$$\alpha \geq \alpha_{cr} = \frac{1}{2}(n^2 - 1)^{\frac{1}{3}}(n^2 + 2)$$

$$\times [C_p(\Delta\omega)_B / \beta n v^2 c] [(\Gamma_L + \Gamma_R) / (\Gamma_L + \Gamma_B)], \quad (1)$$

where n is the index of refraction, C_p and β are the specific heat at constant pressure and the volume expansion coefficient, respectively, $(\Delta\omega)_B$ is the frequency shift of the Brillouin line, v is the speed of sound in the medium, c is the speed of light in vacuum, and Γ_L , Γ_B , and Γ_R are the laser, Brillouin, and Rayleigh linewidths, respectively. A comparison²⁻⁴ of experimental values of α_{cr} with those calculated using Eq. (1) shows considerable disagreement and as a rule calculated values are much larger than the observed ones. For example, the estimated value of α_{cr} for CCl_4 colored with iodine is approximately 0.25 cm^{-1} as compared to an experimentally observed² value of 0.11 cm^{-1} . This difference has been attributed⁴ to nonlinear absorption which does not thermalize rapidly. Although this may turn out to be a valid explanation, one must first accurately ascertain whether the discrepancy is as large as has been quoted in the literature. In this Note, we show that use of the Lorentz-Lorenz law and the low-frequency value for v have made estimates of α_{cr} too high.

In deriving Eq. (1) two principal assumptions have been made which are only approximately true. First, the Lorentz-Lorenz law has been used to approximate the electrostrictive coefficient $\gamma^e \equiv [\rho(\partial\epsilon/\partial\rho)]T$ by $\frac{1}{3}(n^2 - 1)(n^2 + 2)$, where ρ is the density, ϵ the dielectric constant, and T the temperature. It has been shown by Coumou *et al.*⁵ that the Lorentz-Lorenz law yields values for γ^e that are about 10% higher than those determined experimentally. Second, in employing Eq. (1) it seems that dispersion effects have been neglected. It has been pointed out⁶ for the case of linear Rayleigh