MOLECULAR LEVEL-CROSSING SPECTROSCOPY: THE g VALUE FOR AN EXCITED STATE OF NITRIC OXIDE*

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Zero-field level-crossing effects have been optically detected in the nitric oxide molecule by observing the change in intensity of molecular fluorescence from a specified state with magnetic field. The intensity follows an inverted Lorentzian with a field strength at half-maximum of 0.379 ± 0.030 G. Together with the radiative lifetime as recently determined by Jeunehomme, this gives for the molecular g factor for this level a value of 0.762 ± 0.060. This places an upper limit on the magnitude of γ, the molecular ρ-type doubling constant, of $|\gamma| \leq 1.3 \times 10^{-5}$ cm^{-1} (390 KHz).

Level-crossing techniques utilize the changes in the angular distribution of fluorescent light, occurring when two or more energy levels are degenerate to within their natural linewidth, to characterize excited states.[1-3] So far this method has been applied exclusively to the study of atomic systems. An extension of this work to molecules has recently been discussed, suggesting nitric oxide as a possible candidate.[4] We report here the observation of zero-field level crossings in nitric oxide, with the consequent determination of the g value for a specific excited state of that molecule.

When two or more levels are separated by less than their natural linewidth, they may be excited coherently (e.g., by a unidirectional beam of polarized light). The resultant interference terms in emission from such levels manifest themselves in an anisotropic spatial distribution of the fluorescent light. Application of an external field causes changes in the positions of the levels, producing variations in the intensity of the light reaching a detector at a fixed position.

In the experimental arrangement used here (see Fig. 1) the intensity is studied as a function of magnetic field strength. Let the exciting light beam propagate along the X axis and be linearly polarized with its electric vector parallel to the Y axis, as shown in Fig. 1. The behavior of the excited molecule can then be represented to good approximation[4] by a classical dipole also parallel to Y, which radiates after a time τ according to the dipole radiation pattern. Then a photomultiplier located along the Y axis would detect no fluorescent intensity. Suppose now that a magnetic field H is applied in the Z direction, so that the molecule executes Larmor precession about the field direction at a frequency $\omega = g\mu_0 H/\hbar$, where μ_0 is the Bohr magneton. Thus the molecule rotates by an angle $\omega\tau$, on the average, before it radiates. This results in a smearing out of the dipole radiation pattern with a corresponding increase in the detected fluorescent light signal. A more detailed analysis shows that the competition between the rate of precession and the rate of emission causes the molecular fluorescence, when observed using a suitable geometrical arrangement (see Fig. 1), to have an inverted Lorentzian line shape as a function of magnetic field strength. The field strength at half-maximum, $H_{1/2}$, is given by the expression[5]

$$2g\mu_0 H_{1/2}\tau/\hbar = 1, \tag{1}$$

where the molecular g factor is, in general, a function of the quantum numbers of the upper state.

Excitation of the nitric oxide is accomplished using the 2144-Å Cd II ion emission line. This has been shown[6] to excite only the $K' = 13$ ro-

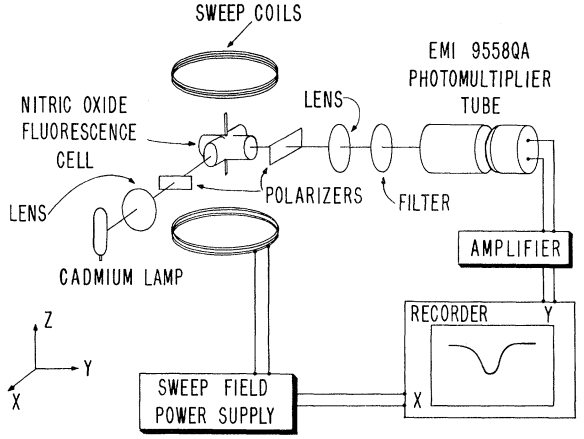

FIG. 1. Experimental arrangement for observation of level crossings in nitric oxide. All quartz optics are used; not shown are coils for cancelling the earth's magnetic field.

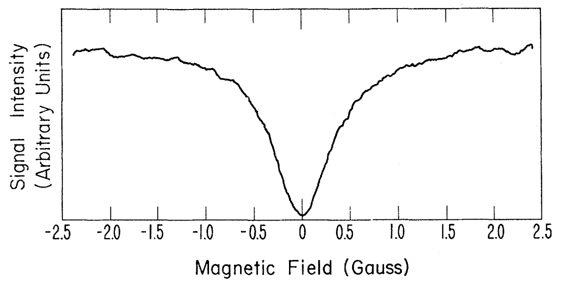

FIG. 2. The magnetic-field-dependent part of the molecular fluorescence as a function of magnetic field strength. This run was taken at 0.069 Torr of nitric oxide.

tational level of the $v'=1$ vibrational level of the $A^2\Sigma^+$ excited electronic state of NO. The light source used was a conventional Philips lamp with the outer jacket removed. Under suitable operating conditions this source appears not to drift by more than ±0.5 % over 3 sec. The polarizers were specially prepared by Polacoat Corporation for this wavelength.[7]

Figure 2 shows a typical line profile, representing a magnetic sweep rate of about $\frac{1}{3}$ G/min with a detector time constant of 3 sec. Because in molecular resonance fluorescence the excited state radiates to vibrational levels other than the ground state, the proper use of an interference filter[8] rejects the scattered exciting light and enhances the signal-to-noise ratio. Linewidths were measured at six pressures covering a range from 0.053 to 0.248 Torr of NO. Although the line shape is asymmetrical at the higher pressures,[9] the linewidth remains constant. Thus we were unable to detect effects of collisional broadening and coherence narrowing[10] in this pressure range.

Using the measured half-width $H_{1/2}=0.379 \pm 0.030$ G, based on 78 runs in all, and Jeunehomme's[11] recently determined value for the radiative lifetime of $(1.965\pm0.03)\times10^{-7}$ sec, we obtain from Eq. (1) a molecular g value of 0.762 ± 0.060 for this excited state of nitric oxide.

A $^2\Sigma$ molecular state, such as considered here, has no electronic orbital angular momentum, and normally is described by Hund's coupling case (b), in which the electronic spin $\vec{S}$ couples to the molecular rotational angular momentum $\vec{K}$. The two levels $K\pm\frac{1}{2}$ are split by the interaction of the electronic spin magnetic moment with the magnetic field produced by the molecular rotation. The size of the splitting is governed by the so-called ρ-type doubling constant γ, and the energy separation is given by

$$\Delta E_\rho = \gamma(K+\tfrac{1}{2}). \qquad (2)$$

The value of γ for the $A^2\Sigma^+$ state of NO is unknown. In the rotational analysis of these bands, Deezsi[12] was unable to detect a splitting even though he observed rotational levels up to $K'=70$. Assuming a spectral resolution of 0.01 cm^{-1} for his instrument, this places an upper limit of $|\gamma| \leq 3\times10^{-4}\ \text{cm}^{-1}$.

If $\vec{S}$ were strongly coupled to $\vec{K}$, the molecular g factor g_K would be reduced from that of a free electron ($g_S=2$) to a value of the order of g_S/K. In our case this would predict $g_K=0.154$. If we also take into account nuclear spin $[I(N^{14})=1;\ I(O^{16})=0]$, the only effect will be to reduce the molecular g factor.

Thus our experimentally determined g value of 0.762 indicates a coupling scheme in between that of a free electron[13] and "pure" case (b) coupling (i.e., an intermediate Paschen-Back region). For this to occur, the ρ-type splitting energy ΔE_ρ must be less than or equal to the magnetic energy $2g\mu_0 H_{1/2}/\hbar$. From Eq. (2) we place an upper limit on the ρ-type doubling constant for the $A^2\Sigma^+$ state of NO of $|\gamma| \leq 1.3\times10^{-5}\ \text{cm}^{-1}$, or 390 KHz. This illustrates the high resolution inherent in molecular level-crossing spectroscopy, whereby we are able to detect energy separations which are a small fraction of the Doppler width at optical frequencies.

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[2] P. A. Franken, Phys. Rev. 121, 508 (1961).

[3] For an example of recent work, as well as references to earlier papers, see W. W. Smith and A. Gallagher, Phys. Rev. 145, 26 (1966).

[4] R. N. Zare, J. Chem. Phys. 45, 4510 (1966).

[5] The factor 2 in Eq. (1) arises from the fact that, with the geometrical arrangement and choice of polarization used here, only levels having $\Delta M=2$ are observed.

[6] H. P. Broida and T. Carrington, J. Chem. Phys. 38,

136 (1963); A. V. Kleinberg and A. N. Terenin, Dokl. Akad. Nauk SSSR 101, 445, 1031 (1955); A. V. Kleinberg, Opt. i Spektroskopyia 1, 469 (1956).

[7] According to a recipe given in M. N. McDermott and R. Novick, J. Opt. Soc. Am. 51, 1008 (1961).

[8] The interference filter shown in Fig. 1 has a peak transmission at 2540 Å with a 150-Å half-width. This passes primarily the $v'=1 \rightarrow v''=4$ vibrational band of the fluorescence.

[9] This is a consequence of the sample being optically thick to the 2144-Å line at the higher pressures, thus distorting the geometry from 90°. See Ref. 3 for a fuller discussion.

[10] An additional advantage of "cross fluorescence" in molecules is that the possible effects of coherence narrowing are reduced by a fraction equal to the branching ratio to the ground vibrational state [see E. B. Saloman and W. Happer, Phys. Rev. 144, 7 (1966), for a discussion of this in the case of atoms]. For nitric oxide, this branching ratio is about 13%, using the intensity measurements of Broida and Carrington, Ref. 6. We wish to thank Dr. A. Lurio for clarification on this point.

[11] M. Jeunehomme, J. Chem. Phys. 45, 4433 (1966).

[12] I. Deezsi, Acta Phys. Acad. Sci. Hung. 9, 125 (1958).

[13] However, some coupling of $\vec{S}$ to $\vec{K}$ must exist in order for us to observe level crossings in a $^2\Sigma$ state using linearly polarized light for excitation. For further discussion see A. Gallagher and A. Lurio, Phys. Rev. Letters 10, 25 (1963).

CHARGE TRANSFER IN THE CLASSICAL BINARY-ENCOUNTER APPROXIMATION*

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Experimental determinations recently have been made[1] of the capture of electrons by protons into the 2*s* state from one- and two-electron systems for incident proton energies ranging from 40 to 200 keV. This note is intended to demonstrate that these measured values can be predicted as well by the classical binary-encounter theory as by any existing quantum mechanical approximations.

We have calculated the cross sections for the reactions

$$H^+ + H \rightarrow H(2s) + H^+, \tag{1}$$

$$H^+ + H_2 \rightarrow H(2s) + H_2^+, \tag{2}$$

$$H^+ + He \rightarrow H(2s) + He^+, \tag{3}$$

using the expression from the Gryziński model[2] for classical binary encounter theory:

$$\sigma = \int_{\Delta E_L}^{\Delta E_U} \sigma_{\Delta E}(v_1, v_2)\, d\Delta E,$$

where $\sigma_{\Delta E}(v_1, v_2)$ is the cross section for energy exchange between an incident charged particle with velocity $\vec{v}_1$ and a bound atomic electron with velocity $\vec{v}_2$, averaged over all orientations of $\vec{v}_2$. The exact expression for $\sigma_{\Delta E}$ has been given by Gerjuoy,[3] and is easily integrated. For the integration limits we use the simple expression given by Gryziński,[2]

$$\Delta E_L = \tfrac{1}{2} m_e v_1^2 + U_A - U_B,$$

$$\Delta E_U = \tfrac{1}{2} m_e v_1^2 + U_A + U_B,$$

where U_A is the binding energy of the electron in the target atom and U_B is the binding energy of the electron after capture. The resultant expression is to be multiplied by the number of equivalent electrons. It should also be averaged over the speed distribution of the target electron; we have used a delta-function distribution only: $f(|\vec{v}_2|)$ proportional to $\delta(v_2 - [2U_A/m_e]^{1/2})$. The primary assumptions of our model are then the following: (a) The interaction between the electron and the incident proton is the primary one in determining this cross section; (b) the incident proton's trajectory is essentially unaffected by the process; and (c) the magnitude of the energy transfer is the primary criterion for deciding whether or not capture occurs.

Of these assumptions, (c) is the weakest, since not all electrons whose energies after collision are in the correct energy range for capture will be captured; capture is not equally probable for all directions and magnitudes of the electron momentum relative to the proton. Taking the electron momentum into account has been attempted.[4] The major effect is a more rapid decrease of the cross section at high energies, which in the present model is proportional to $1/E^3$. For the relatively low energies of these measurements, however the weaker assumption may suffice. Assumption (c) is not entirely independent of assumption (a), since classically the target atom-electron interaction provides the mechanism for