



## Energy of the A 1 $\Delta$ state of ZrO

Philip D. Hammer, Sumner P. Davis, and Alma C. Zook

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COMMUNICATIONS

# Energy of the A <sup>1</sup>A state of ZrO

Philip D. Hammer and Sumner P. Davis

Physics Department, University of California, Berkeley, California 94720

Alma C. Zook

Physics Department, Hamilton College, Clinton, New York 13323 (Received 6 February 1981; accepted 16 February 1981)

Until recently there has been uncertainty as to the energies of the low-lying states of ZrO. The singlettriplet separation was recently determined,<sup>1</sup> and now the energy of the  $A^{1\Delta}$  state has been established. A calculation using molecular orbital theory<sup>2</sup> placed it 5000 cm<sup>-1</sup> above the  $X^{1\Sigma}$  ground state, while an experimental value of 5200 cm<sup>-1</sup> was obtained from Ne matrix spectra.<sup>3</sup> We have observed laser -excited fluorescent transitions in the vapor phase, from the  $B^{1}\Pi$  state to several lower-lying states. These transitions together with a subsequent rotational -vibrational analysis of the B-Asystem<sup>4</sup> yield a value for  $T_e(A^{1}\Delta)$  of 5904.19 cm<sup>-1</sup>. Note that we are using the electronic state designations of Huber and Herzberg.<sup>5</sup>

Details about the source, spectrometer, laser, and experimental method are similar to those of previous work.<sup>1,6</sup> To summarize,  $ZrO_2$  powder was heated to 2700 K in a King-type furnace. A buffer gas of helium was kept at a pressure of less than 3 Torr to minimize collisional quenching of the excited states. The dye laser was operated in the cw mode with an output of 100 mW and a linewidth of less than 0.005 nm. The spectra were recorded on the appropriate sensitized photographic plates (Kodak I-Z, 121-01, or I-N) at a typical plate factor of 0.04 nm/mm. Exposures ranged from 10 to 45 min.

The laser was tuned to excite the (1-0) R head of the  $B^{1}\Pi - X^{1}\Sigma^{+}$  system at 615.43 nm,<sup>7</sup> thereby populating a sequence of levels of  $B^{1}\Pi_{e}$  with v = 1 and J = 15 to 20. The e symmetry P and R transitions are the only branches allowed by selection rules. Only <sup>90</sup>Zr<sup>16</sup>O was excited, since the next nearest R head ( ${}^{91}$ ZrO) is 0.026 nm to longer wavelengths and the bands are red degraded. We then looked for sequences of consecutive rotational transitions in fluorescence, and were able to observe such transitions in the (1-0) and (1-1) bands of the B-A system, as well as in the (1-0), (1-1), (1-2), (1-3), and (1-4) bands of the B-X system. Transitions to the (1-0) band of the B-A system are listed in Table I. These results, together with the more extensive analysis mentioned above, <sup>4</sup> yield a value for  $T_e(A^{1}\Delta)$  of 5904.19 cm<sup>-1</sup> above the ground state, for  $^{90}$ Zr<sup>18</sup>O.

Fluorescent transitions were also observed to the  $a^{3}\Delta_{2}$  state, and these measurements confirm an earlier value for  $T_{e}(a^{3}\Delta_{1})$  of 1099.08 cm<sup>-1</sup> above the ground state.<sup>1</sup> The relevant observational data are listed in Table II.

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| TABLE I. Observe                       | d fluorescence of the (1-0) |
|--|-----------------------------|
| band of $B^{1}\Pi_{e} - A^{1}\Delta$ . | Wave number units are       |
| em <sup>-1</sup> .                     |                             |

| $J^{\prime\prime}$ | Р         | Q         | R          |
|--------------------|-----------|-----------|------------|
| 14                 | •••       | •••       | 10 358.193 |
| 15                 | •••       | 10345.700 | 10358.480  |
| 16                 | 10332.388 | 10345.164 | 10358.730  |
| 17                 | 10331.011 | 10344.581 | 10358.951  |
| 18                 | 10329.596 | 10343,970 | 10359.138  |
| 19                 | 10328.158 | 10343.321 | 10359.303  |
| 20                 | 10326.673 | 10342.657 | 10359.432  |
| <b>21</b>          | 10325.180 | 10341.951 | •••        |
| 22                 | 10323.643 | • • •     |            |

TABLE II. Observed intercombination fluorescence of the (1-1) band of  $B^{1}\Pi_{e}-a^{3}\Delta_{2}$ . Wave number units are cm<sup>-1</sup>.

| J''       | Р           | Q           | R                  |
|-----------|-------------|-------------|--------------------|
| 15        | • • •       | •••         | 13 947.109         |
| 16        |             | 13 933, 904 |                    |
| 17        | 13919.872   | 13 933.453  | • • •              |
| 18        | •••         | 13 932, 964 | •••                |
| 19        | 13 917, 292 | 13 932.471  | 13 <b>9</b> 48,435 |
| 20        | 13 915, 963 | 13 931, 928 | •••                |
| <b>21</b> | 13 914, 592 | •••         | • • •              |

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# Can photochemistry be enhanced on rough surfaces?

Abraham Nitzana) and L. E. Brus

Bell Laboratories, Murray Hill, New Jersey 07974 (Received 6 November 1980; accepted 18 February 1981)

Recent work<sup>1</sup> has shown that at least part of the surface enhanced Raman phenomenon<sup>2</sup> (SERS) is due to the intensified local electromagnetic field which occurs near a surface protrusion  $(10-10^3 \text{ Å scale})$  on a rough surface. Incident fields are locally enhanced near the protrusion by image, shape, and plasmon resonance effects. Consequently, all types of electromagnetic interactions should be affected. Indeed, enhanced absorption and subsequent luminescence have recently been reported.<sup>3-5</sup>

This communication addresses the question of whether photochemical processes may also be enhanced. Enhanced absorption does not necessarily imply enhanced photochemistry because of the existence on the surface of competing routes for molecular energy dissipation. These are (a) radiationless transfer of molecular energy to the surface and (b) thermal and photon induced desorption of adsorbed molecules. It is therefore necessary to study the time scale and the efficiency of the photochemical process relative to these competing channels. It is also necessary to find and model dielectric materials with resonances throughout the IR-UV photochemical range.

To investigate the feasibility of surface enhanced photochemistry we study a classical molecular dipole at a distance from the surface of a dielectric sphere of radius *a* and dielectric function  $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ . The molecule is modeled as a polarizable point dipole with characteristic frequency  $\omega_0$ . Both *a* and *d* are much smaller then the field wavelength  $\lambda$ . The equations of motion for the molecule and the dipolar modes of the sphere are<sup>7</sup>

$$\ddot{R} + \omega_0^2 R + \Gamma \dot{R} = \frac{1}{m} \frac{\partial \mu}{\partial R} \cdot (\mathbf{E} + \vec{M} \mu_1) , \qquad (1a)$$

$$\ddot{\mu}_{1} + 2\gamma_{1}\dot{\mu}_{1} + (\omega_{1}^{2} + \gamma_{1}^{2})\mu_{1} = \alpha_{1}(\omega_{1}^{2} + \gamma_{1}^{2})(\mathbf{E} + \vec{M}\,\mu) , \qquad (1b)$$

where R,  $\mu(R)$ , m, and  $\omega_0$  are the intramolecular coordinates, and the associated molecular dipole, mass, and transition frequency, respectively. For vibrational excitation  $\omega_0^2 R$  may be replaced by  $(1/m)\partial V(R)/\partial R$ , where V(R) is the intramolecular potential; for atomic transitions  $|\mu(R)| = e |R|$ , e and m being electronic charge and mass, respectively.  $\mu_1$  is the dipole induced on the sphere,  $\omega_1$  is the solution to  $\epsilon_1(\omega_1) = -2$ ,  $\gamma_1 = \epsilon_2(\omega_1)/\epsilon_1'(\omega_1)$ , and  $\alpha_1 = 6a^3\omega_1/[(\omega_1^2 + \gamma_1^2)\epsilon_1'(\omega_1)]$ .  $\mathbf{E} = \mathbf{E}_0 \cos \omega t$  is the

incident field, and  $\overline{\mathbf{M}} = (3\hat{n}\hat{n} - \overline{\mathbf{I}})/(d+a)^3$ , where  $\hat{n}$  is a unit vector along the molecule-sphere center axis. Here  $\epsilon'_1 = \partial \epsilon_1 / \partial \omega$ . Finally,  $\Gamma = \Gamma_0 + \Gamma_1$  is the molecular decay rate.  $\Gamma_0$  is the free molecule term and  $\Gamma_1$  (analogous to the surface induced decay term of molecule near a plane surface<sup>8</sup>) arises from the interaction of the molecule with all the nonradiative (l > 1) sphere modes.<sup>7</sup> These equations describe two coupled Drude dipoles in an external field. Equation (1b) is approximate and applies when  $\omega_1$  is not too different from  $\omega$ . All the parameters in Eqs. (1) are estimated from available spectroscopic data.

We now consider two examples:  $I_2$  photodissociation near 4500 Å is a one-photon process with a short (~10<sup>-14</sup> sec) excited state lifetime. We simulate the continuous  $I_2$  absorption by a broad Lorentzian resonance. Figure 1 shows the steady-state absorption line shape [e.g.,



FIG. 1. Effective absorption cross section vs incident frequency for a model of  $I_2$  photodissociation. d is the distance from the surface of a silver sphere of radius a = 500 Å. The molecular dipole lies along sphere radius.

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