Collective Rotor-Vibrator Spectra in Alkaline-Earth Atoms

Michael E. Kellman
Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

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Energy-level patterns of He**, Be, Mg, Ca, Sr, and Ba are compared to the spectrum of a linear rotating *ABA* molecule with bending vibrations. The spectra of the alkaline earths are found to agree with the rotor-vibrator model even better than the spectrum of He**, the system for which the molecular model was originally proposed.

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In 1978, Kellman and Herrick[1] proposed that some levels of doubly excited helium (He**) had a spectrum resembling that of a linear rigid rotor. They suggested that electron correlation in these states is so strong that a linear, quasirigid *e*-α-*e* structure gives a better picture than the usual independent-particle model. In 1980, Herrick and co-workers[2–5] greatly extended this picture to include bending vibrations as well as overall rotation of the quasirigid structure. The *e*-α-*e* system thus has a spectral pattern similar to that of a linear *ABA* triatomic molecule. This rotor-vibrator pattern was found in Refs. 2–4 with the help of an SO(4) "supermultiplet" classification of the atomic terms.

The advent of the rotor-vibrator model is obviously a drastic departure from traditional notions of electronic structure. The ultimate significance of this atomic collective model will be greater, however, if it is applicable to atoms with more than two electrons, or for systems less exotic than doubly excited helium. In this communication, I analyze alkaline-earth spectra and find that they do in fact show the energy-level patterns characteristic of the rotor-vibrator model. In fact, the spectra of the alkaline earths are in some respects in *better* agreement with the rotor-vibrator model than is He**.

It is interesting that in a recent communication, Krause and Berry[6] report that some states of alkaline earths have spatial distributions indicative of a highly correlated structure for the valence electrons. This follows earlier work of Berry and co-workers[7] on spatial distributions of He** which amply confirmed the evidence of the supermultiplet rotor-vibrator classification.

We begin by recalling in Fig. 1 the rotor-vibrator supermultiplet classification for experimental levels[8] of He** with both electrons in the $n=2$ shell. These six terms in independent-particle language are the $2s^2\,{}^1S^e$, $2s2p\,{}^1P^o$; $2s2p\,{}^3P^o$, $2p^2\,{}^3P^e$; and $2p^2\,{}^1S^e$, $2p^2\,{}^1D^e$. In the rotor-vibrator classification, they are labeled by the quantum numbers $(v_2, |l|, J)$ for bending vibration excitation v_2, projection of angular momentum $\pm l$ along the figure axis, and total angular momentum J. Figure 1 shows the same terms for the ns^2, $nsnp$, and np^2 levels of Be, Mg, Ca, Sr, and Ba with energies taken from the tables of Moore.[9] Clearly, these alkaline-earth levels have the same overall pattern as He**, consistent with the rotor-vibrator model, and also with the spatial distributions of Ref. 7. (Some of the assignments of Ref. 9 have been challenged. Some authors[10,11] place the Ba $2p^2\,{}^1S^e$ at 38 664 cm^{-1} instead of 34 371; Aymar and Robaux[12] place the Ba $2p^2\,{}^1D^e$ at 38 556 instead of 35 344. However, for our purposes, the configuration assignments may not matter anyway, since the collective model implies strong configuration mixing. In any case, the higher term energies for these Ba levels would not much alter Figs. 1–3 or the following discussion.)

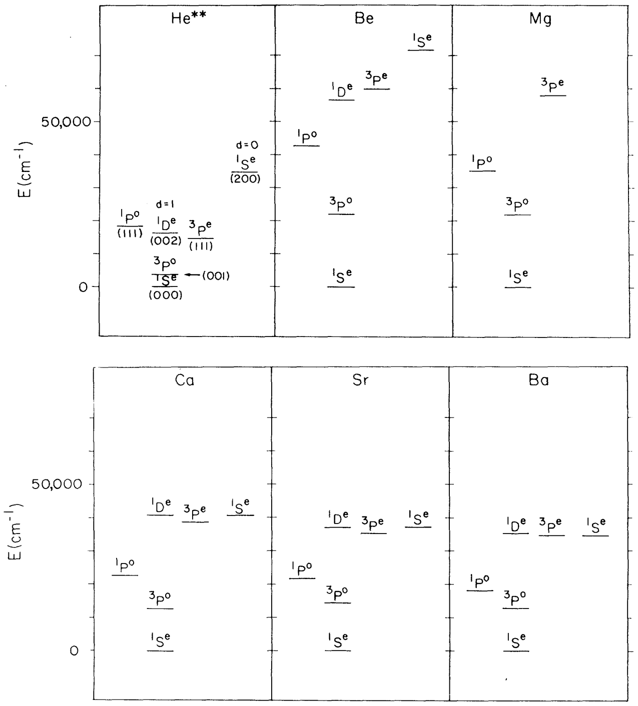

FIG. 1. Rotor-vibrator classification of ns^2, $nsnp$, and np^2 terms of atoms with two valence electrons. At the top left are shown experimental levels (Ref. 8) of He** with terms grouped into the $d=1$ and $d=0$ supermultiplets of Refs. 2–4. Each term is labeled by the approximate rotor-vibrator quantum numbers $(v_2, |l|, J)$. The alkaline-earth levels (Ref. 9) are classified in the same way. The $2p^2\,{}^1D^e$ and ${}^1S^e$ levels of Mg are not given in Ref. 9 and are absent in the figure.

Let us therefore examine quantitatively the similarities (and differences) among the alkaline earths, He**, and the *ABA* rotor-vibrator. First, in Fig. 2 the $^1S^e, ^3P^o, ^1D^e$ "rotor series" of each species is compared with the spectrum of an exact rigid rotor. The figure shows that He** has a rotational constant that increases with J, as pointed out in Refs. 1 and 4. In contrast, for the alkaline earths, the rotational constant decreases with J. A decreasing moment of inertia is the behavior typical of polyatomic molecules. In addition, the alkaline-earth rotor series are, if anything, quantitatively closer to the pure rigid-rotor spectrum than is He**. The first conclusion is therefore that the alkaline-earth rotor spectrum is in even better agreement with the molecular model than is He**.

Next, we test the alkaline-earth spectra against the molecular picture of near-harmonic bending vibration. To do this, we compare the energies of the levels labeled $v_2=1, l=\pm1$ and $v_2=2, l=0$ in the molecular model. In molecules it is well known that the $l=\pm1$ levels are split[10] because of the effect of "l doubling." The atomic levels corresponding to $v_2=1, l=\pm1$ are the terms $^3P^e$ and $^1P^o$, and in Fig. 1 these certainly show l doubling, as was noted in Refs. 2–4 for He**. We therefore take the energy for $(v_2, |l|, J)=(1,1,1)$ as the average of the $^3P^e, ^1P^o$ terms.

At first glance, it appears that the (1,1,1) and (2,0,0) levels for the spectra of Fig. 1 agree with the harmonic bending model reasonably well for He**, less well for Be, and not at all for the heavier species. However, in the rotor-vibrator picture, these levels have both rotational and vibrational contributions, and we must distinguish between these for a meaningful evaluation of the vibrational component itself. We therefore use a standard leading-order formula for the levels of a molecular rotor-vibrator:

$$E(v_2,l,J)=E_0+\omega(v_2+1)+\alpha(v_2+1)^2 +\beta J(J+1)+\gamma l^2 . \quad (1)$$

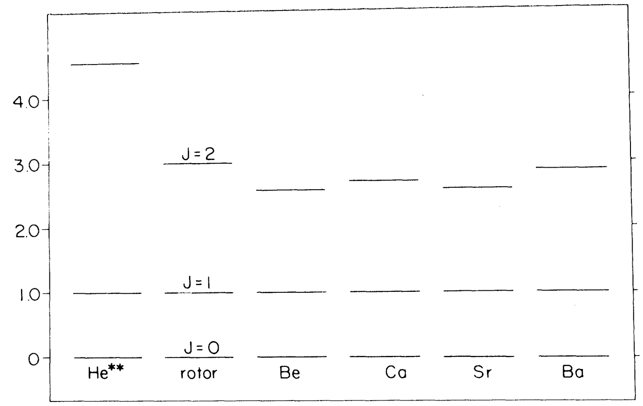

FIG. 2. The "rotor series" for He** and alkaline earths. They are compared to the spectrum of a rigid rotor, with the $^1S^e$-$^3P^o$ excitation energy normalized to unity.

Apart from the additive constant E_0, this formula includes parameters ω for the harmonic bending frequency, α for the anharmonicity, and β,γ for the rotational energy of a symmetric top. (It does not, however, contain an l-doubling term.) We have already seen good agreement in Fig. 2 with this formula for the "rotor series," with $v_2=l=0$. To use Eq. (1) to test the hypothesis of bending vibrations, we now take into account for the $v_2=1$, $|l|=1$ level the presence of the angular momentum contribution $2\beta+\gamma$ in addition to the purely vibrational component $2\omega+4\alpha$. We take the overall rotational constant β as the difference $E(0,0,1)-E(0,0,0)$ of the $^3P^o$ and $^1S^e$ rotor levels. Next, a rough approximation for γ is to take $\gamma=-\beta$. This treats γl^2 as a correction to the rotor term $\beta J(J+1)$, whereby the projection of angular momentum along the linear axis is taken to have a negligible rotational constant.

We can now separate out the pure vibrational component $\omega(v_2+1)+\alpha(v_2+1)^2$ in the (1,1,1) and (2,0,0) levels, and determine the harmonic zero-order bending frequency ω and the anharmonicity parameter α. The vibrational spectra obtained in this way are shown in Fig. 3. The values of the crucial ratio α/ω are listed in Table I. Both the figure and the table show that the alkaline earths are closer to the pure harmonic limit than is He**. In addition, the sign of α/ω is negative for alkaline earths, in agreement with the usual behavior in molecules and in contrast with He**. The second conclusion is therefore that the alkaline-earth spectra are in even better agreement with the bending vibration model than is He**.

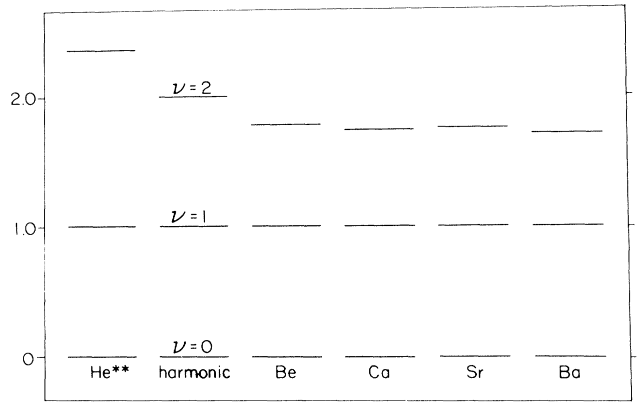

FIG. 3. Bending vibration energies of atomic species compared to a harmonic vibrational progression. The energy of the first vibrational level is normalized to unity. As discussed in the text, vibrational energies are determined first by averaging energies of l doublets, then removing the rotational component of the energy to obtain the vibrational contribution alone.

We now examine more closely the l doubling which splits the $v_2=1, l=\pm1$ levels. In Fig. 1 the $^3P^e$ is lower in energy for He** and higher for the alkaline earths. From comparison with the diagrams of Herzberg,[13] this sign of

TABLE I. Ratios of α/ω of the anharmonicity parameter α and harmonic zero-order energy ω [cf. Eq. (1)].

Atom	α/ω
He**	0.394
Be	−0.082
Ca	−0.095
Sr	−0.092
Ba	−0.102

TABLE II. Values of the nonrigidity parameter γ' [cf. Eq. (2) and Ref. 16]. For highly nonrigid systems, $\gamma'=1$; for a completely rigid system, $\gamma'=0$.

Atom	γ'
He**	0.207
Be	0.615
Ca	0.745
Sr	0.771
Ba	0.714

the l doubling for alkaline earths is the same as is typical for *ABA* triatomics, again indicating better agreement than for He** with the molecular model. The relative magnitude of the l doubling is greater for the alkaline earths than for He**. In itself, this is evidence neither for nor against the rotor-vibrator model. It may be significant, however, that in all cases the magnitude of the l doubling is about the same as the energy $E(0,0,1)-E(0,0,0)$ of the first rotor excitation. Molecular l doubling is proportional[14] to β^2/ω, and so is expected to be greater when the rotational constant β is relatively large, as with the alkaline earths. (Crance and Armstrong[15] have investigated the sign and magnitude of the splitting in He**.)

As the final comparison among atomic species, let us seek a quantitative measure of their relative degree of nonrigidity. One very simple index is suggested by the "nonrigidity parameter" of Amar, Kellman, and Berry[16] for nonrigid molecules. The work of Kellman[17] on XY_2 nonrigid molecules is more directly related to the case of two valence electrons, and suggests as a nonrigidity parameter

$$\gamma'=2E(0,0,1)/E(2,0,0)\,, \tag{2}$$

relating the energy of rotational to vibrational excitation. For very rigid molecules, this approaches 0; for highly nonrigid molecules, 1. Table II lists γ' and shows that all the atomic species are quite nonrigid, with He** distinctly more rigid than the alkaline earths. This is not surprising since the alkaline earths contain a spherical electron core, while He** does not. It is auspicious for the future application of collective models to many-electron atoms that the alkaline earths conform better to the rotor-vibrator pattern, despite their having a large core. This is perhaps not so surprising, however, when one considers that nuclei have very sharp collective features even though they are highly nonrigid systems. It is also possible that the higher nonrigidity of alkaline earths is related to their large l doubling. Since molecular l doubling is caused by rotation-vibration interaction, it might be expected to be larger for nonrigid systems.

The final point concerns terms such as $4s\,3d$ for Ca which do not fit into the supermultiplet scheme. The supermultiplet classification of He** was based on the fact that single-particle manifolds with a given n such as $(2s,2p)$ or $(3s,3p,3d)$ form nearly degenerate SO(4) multiplets. This is clearly not the case in general for many-electron atoms. One might, however, try to group, say, the $(4s,3d,4p)$ orbitals for Ca into a nine-dimensional SO(4) multiplet. One would then try to fit these into a supermultiplet classification for $(4s,3d,4p)^2$ terms. However, comparison with the energy levels of Moore shows strong perturbation of this larger supermultiplet pattern. The success of the rotor-vibrator model for the $(ns,np)^2$ subspace therefore may indicate that a different role is played by the $(n-1)d$ subshell. It is significant in this regard that in Ref. 6 it is found that the $4s\,3d$ "interloper" state of Ca seems not to have a place in the molecular picture of electronic spatial distributions. On the other hand, the highly perturbed supermultiplets obtained in the full $(4s,3d,4p)^2$ space may simply be due to the combined effects of l doubling, strong rotation-vibration mixing, and anharmonicity for higher values of the molecular quantum numbers. The role of the interloper states in the collective model therefore needs to be explored further.

In summary, energy-level patterns for the ns^2, $nsnp$, and np^2 terms of alkaline earths show agreement with the rotor-vibrator model which is qualitatively and quantitatively better than for the He** system. Investigation of collective behavior for multielectron atoms, including systems with more than two valence electrons, is now a challenge of extreme interest. A method to elucidate these spectral patterns will be the subject of a future paper.

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