

ELECTRIC FIELD SPECTROSCOPY OF ULTRACOLD POLAR MOLECULAR DIMERS

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We propose a novel kind of electric field spectroscopy of ultracold, polar molecules. Scattering cross sections for these molecules will exhibit a quasi-regular series of resonance peaks as a function of applied electric field. In this contribution, we derive a simple approximate formula for $F(n)$, the electric field F at which the n th resonance appears.

The topic of this contribution does not strictly belong at the International Conference on Laser Spectroscopy, I suppose, since it has nothing whatever to do with lasers. However, I do intend to discuss a kind of spectroscopy that is peculiar to polar molecules in an ultracold environment. It turns out that polar molecules at low temperatures respond really strongly to electric fields, particularly when the molecules collide. So, by monitoring the scattering cross section as a function of electric field, you can try to read out information on the dimer formed by the collision partners. In what I discuss here, I consider the effect of a dc field; you could think of it as a kind of “dc laser spectroscopy,” if you like.

Consider a pair of molecules that approach one another in an ultracold environment, with essentially zero relative kinetic energy. The actual scale of this energy is assumed to be something like milliKelvin, or perhaps tens of microKelvin; it depends on whose experiment you’re talking about [1]. Considering that ten microKelvin corresponds to something like 200 MHz of energy, a cold collision event could in principle probe resonant structure between the colliding partners on about this scale. This is plenty enough resolution to distinguish between different ro-vibrational states, for example.

Well, there’s an obvious problem with using these collisions for spectroscopy. The collision energy, within this temperature-defined width, is always the same, namely, zero. This seems to imply that you could probe one very tiny slice of the collisional spectrum really well, but at the expense of *everything else* going on in the complex. In conventional spectroscopy, this would not be a problem, since you could bring in photons of a desired energy and raise or lower the energy of the collision partners to any other energy level

you want to probe. (In the context of cold collisions, this is in fact done frequently, and is known as photoassociation [2].)

There is an alternative way to proceed, however. Rather than driving the molecules to a bound state at a different energy, you could instead shift the energy of the bound state until it coincides with the energy of the molecules, i.e., zero. This is not completely crazy, or at least it's not without precedent. For years now experimenters have been using magnetic-field Feshbach resonances in alkali atoms to make resonant states coincide with the threshold of the scattering continuum. This has been a very fruitful tool for engineering the mean-field interaction energy of ultracold gases, but it is something else, too. For a realistic two-body interaction potential to reproduce such a resonance at the correct field is quite a severe constraint on the potential [3]. The point is, field variation of cold collision cross sections can really be a useful probe of the interaction, i.e., a spectroscopic tool.

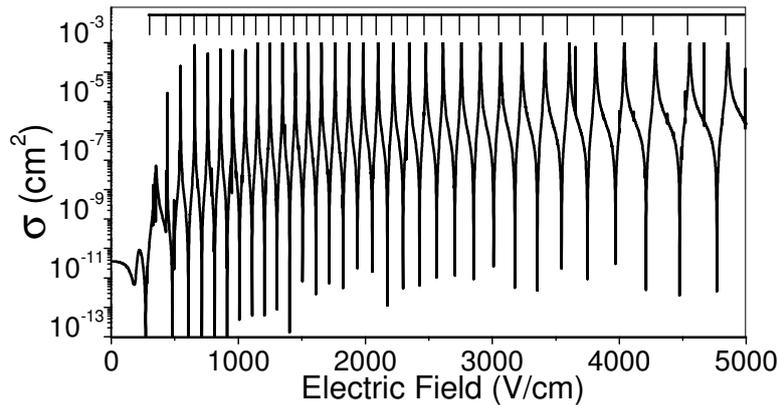


Figure 1. Elastic scattering of SrO molecules at a collision energy of 10^{-12} K, as a function of electric field. This scattering produces a surprisingly regular series of resonances.

The effect of an *electric* field on *polar* molecules is likely to be much more profound, since electric forces are generically stronger than magnetic forces in molecules. And sure enough: in Figure 1 I show the electric-field-dependent elastic scattering cross section of ultracold SrO molecules. These molecules are assumed to be in their electronic ($^1\Sigma$), vibrational ($v=0$), and rotational ($J=0$) ground states, and to collide at an energy of 10^{-12} K. This figure is reproduced from our recent study of electric field resonances [4], and the details of the scattering model are explained there.

The main point of figure 1 is that the cross section is dominated by a strikingly regular series of resonances. In Ref. [4] we explain that these

resonances originate in the purely long-range dipole-dipole interaction between the molecules. Roughly, the field can change the degree of polarization of the molecules, hence their dipole-dipole interaction. Ref. [4] also shows that the exact position and spacing of the resonances carries information about the “short-range” physics, where the molecules actually collide and probe their potential energy surface. (Also appearing in this figure, although far less prominent, are various Feshbach resonances that describe excitation to higher-lying rotational and fine-structure states. Obviously they will also carry information about the interaction that excited these degrees of freedom.)

This discussion should sound vaguely familiar. The backbone of atomic spectroscopy is the Rydberg series. Any atom with a singly-excited electron has a spectrum of energy levels that scales as $-1/n^2$. Well, no, of course that’s not true. In fact, the spectrum of such an atom scales as $-1/(n-\mu)^2$, where μ is a quantum defect [5]. The role of the quantum defect, as all good spectroscopists know, is to encode the electron’s interaction with all the other electrons in the parent ion. The entire series of energy levels is described by a simple formula that is flexible enough to apply to any atom.

What I would like to do here is to derive an analogue of the Rydberg formula for an electric-field spectrum like the one in Figure 1. In other words, I would like an analytic expression $F(n)$ that gives the electric field value F at which the n th resonance is observed. This will not be the world’s greatest derivation, but it will get the basic physical ideas right.

Let’s first note the following. In spectra such as that in Fig.1 that I’m considering, the collision energy is nearly zero, and it is the electric field that is being scanned. The resonant state therefore extends to infinite intermolecular separation R . In this case, the relevant interaction potential is described by the largest- R part of the adiabatic potential energy curve. Well, we’ve discussed the form of this curve previously [6]. The lowest potential, the one that carries the resonances, is mostly s-wave in character (i.e., it has partial wave angular momentum $l=0$). But the dipole-dipole interaction vanishes by symmetry for s-waves, so the only effect of the dipolar interaction is to mix s-waves with nearby d-waves ($l=2$).

It turns out that this means two things. First, in zero field the effective interaction scales as $-C_6/R^6$. Second, in nonzero field, the interaction quickly turns over to a $-C_4/R^4$ behavior, where the effective C_4 coefficient is given by [6]

$$C_4 = \left(\frac{\eta^2}{1+\eta^2} \right)^2 \frac{\mu^4 m_r}{\hbar^2}. \quad (1)$$

Here $\eta = 2\mu F / \Delta$ represents the electric field F in units of the critical field $F_0 = \Delta / 2\mu$ that separates the quadratic and linear Stark effect regimes; Δ is the energy splitting between the given rotational level and the next higher one; and m_r is the reduced mass of the collision partners. Equation (1) includes only the

perturbation due to the $l=2$ partial wave, but you can easily extend it to higher partial waves, if you like. Notice that the value of C_4 saturates as you go to the high-field limit $F \gg F_0$. Well, of course: once the molecules are polarized, the field can't do much more to change the situation. (I do not consider here fields large enough to distort the electronic wave functions, which would be another story.)

Since I'm talking here about field-dependent resonances, I will concentrate on the field-dependent $1/R^4$ part of the interaction. At zero collision energy, the WKB phase for this potential is easily calculated. To identify a bound state, you set this phase equal to an integral multiple of π

$$\phi_{WKB} = \int_a^\infty dR \sqrt{\frac{2m_r C_4}{\hbar^2 R^4}} = \frac{\sqrt{2} \mu^2 m_r}{a \hbar^2} \left(\frac{\eta^2}{1+\eta^2} \right) = n\pi. \quad (2)$$

Here I have imposed an arbitrary small- R cutoff radius, a . And it's a good thing, too, since the integral would diverge if I were to let $R \rightarrow 0$. But anyway, the potential is clearly not proportional to $1/R^4$ all the way to small R , and besides, whatever goes on for $R < a$ is going to be accounted for in the quantum defect.

Now you could just invert (2) to find the resonant field at which the n th bound state appears. As a fitting formula, this leaves something to be desired, however, since the result would depend explicitly on the unphysical cutoff radius a . A better use of the quantization condition would be to exploit the saturation behavior, and to write

$$\frac{\eta^2}{1+\eta^2} = \frac{n}{\tilde{n}_\infty}, \quad (3)$$

where $\tilde{n}_\infty = \sqrt{2} \mu^2 m_r / \pi a \hbar^2$ is the approximate total number of bound states in the potential in the limit of large electric field. In other words, when the field is large, $\eta \rightarrow \infty$ and $n \rightarrow \tilde{n}_\infty$. Having made this correction, *then* you could then invert (3) to find the set of resonant field values $F(n)$.

Oh no, wait, I'm sorry, there is one more thing. In practice, it's more useful to append the quantization condition (3) to read

$$\frac{\eta^2}{1+\eta^2} = \frac{n+n_0}{\tilde{n}_\infty}. \quad (4)$$

In this expression, n_0 / \tilde{n}_∞ represents the additional part of the phase shift arising from the short-range part of the potential. Here is our analogue of the quantum defect. Finally, when you *do* actually invert the expression (4) to find the resonant fields, you get

$$F(n) = F' \sqrt{\frac{n_0 + n}{\tilde{n}_\infty - n}}. \quad (5)$$

where $n_\infty = \tilde{n}_\infty - n_0$, and F' is expected to be on the order of F_0 .

Does this work? Surprisingly, yes. Look at Figure 2, where I have plotted the resonant fields $F(n)$ versus n for both the SrO example in Fig.1, and for RbCs. In both cases I have fit to the formula (5), and shown the results as solid lines. The fit is not half bad, and clearly gets the general form of the spectrum correct.

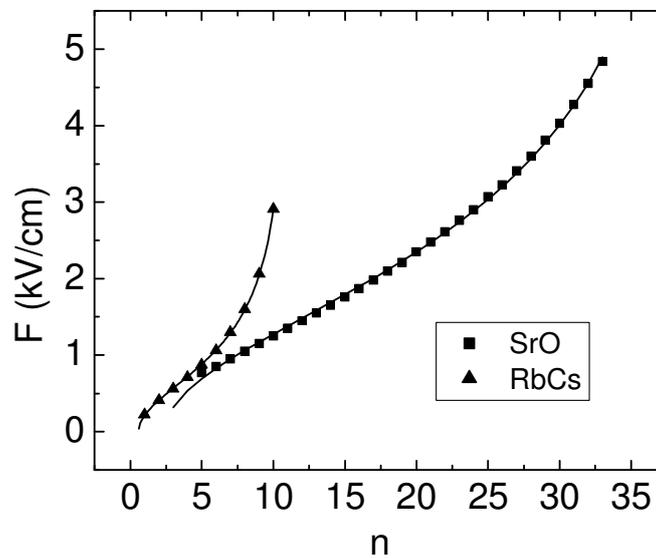


Figure 2. Electric field values $F(n)$ at which the n th resonance occurs, as seen in close-coupled calculations of SrO (squares) and RbCs (triangles) cold collisions. Solid lines represent fits to the formula in Eqn. (5).

A few remarks are in order. First, the actual value of n is pretty arbitrary, since I have no idea how many bound states there really are. In fact, I have anchored the calculation in the final number of bound states after the field has saturated the interaction. Therefore, it actually makes more sense to count the resonances “backwards,” from n_∞ down. (Note that n_∞ need not be an integer, of course.) This is actually a typical way to count the very most weakly-bound states of potentials [7].

Second, the assumption that the long-range potential scales with R as $1/R^4$ is not true at zero field. Thus, in order to get a suitable fit for the RbCs spectrum, I had to ignore the first four calculated resonances. Third, by no means is (5) intended to be a rigorous result. Rather, it is a simple and comfortable way to

characterize the series in a simple formula. It should, for example, provide an estimate of how many resonances to expect for a given molecule in a given field range. Plus, it strongly suggests that there *should exist* a simple formula. Someday somebody should go back and find the correct formula in a more rigorous way.

Acknowledgments

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