

# A scaling rule for molecular electronic transition dipole moments

**Citation for published version (APA):**

Johnston, C. W., & Mullen, van der, J. J. A. M. (2003). A scaling rule for molecular electronic transition dipole moments. *Journal of Chemical Physics*, 119(4), 2057-2061. <https://doi.org/10.1063/1.1582851>

**DOI:**

[10.1063/1.1582851](https://doi.org/10.1063/1.1582851)

**Document status and date:**

Published: 01/01/2003

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

**General rights**

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

[www.tue.nl/taverne](http://www.tue.nl/taverne)

**Take down policy**

If you believe that this document breaches copyright please contact us at:

[openaccess@tue.nl](mailto:openaccess@tue.nl)

providing details and we will investigate your claim.

# A scaling rule for molecular electronic transition dipole moments: Application to asymptotically allowed and forbidden transitions

C. W. Johnston and J. J. A. M. van der Mullen<sup>a)</sup>

*Department of Applied Physics, Eindhoven University of Technology, Eindhoven, The Netherlands*

(Received 5 August 2002; accepted 25 April 2003)

Guided by the work of Woerdman and Monyakin, we propose rules that allow the electronic transition dipole moment for a transition in one molecule to be determined from that of a similar one in an isovalent species. The rule can be applied to asymptotically allowed and forbidden transitions. We have tested it by applying it in two specific cases: the moments for the  $A^1\Sigma \rightarrow X^1\Sigma$  and  $X^1\Sigma \rightarrow B^1\Pi$  transitions in  $\text{Na}_2$  are found from those in  $\text{Li}_2$ , which are asymptotically allowed and the moments for the  $B \rightarrow X$  transition in  $\text{O}_2$ ,  $\text{Se}_2$ , and  $\text{Te}_2$  which are asymptotically forbidden, are found from moment data for  $\text{S}_2$ . Transition moments calculated with this rule are within 15% of the available literature values and behavior as a function of internuclear separation is well described.

© 2003 American Institute of Physics. [DOI: 10.1063/1.1582851]

## I. INTRODUCTION

The electronic transition dipole moment (ETDM) is an especially important term in the spectroscopy of diatomic molecules as it determines the strength of a particular transition. Detailed knowledge of it can be useful not only in diagnostics but also in discharge modeling where it can be employed in the simulation of spectra as well as the determination of electron impact excitation cross sections. While ETDM data are available in the literature, certainly not all transitions that might be of interest are represented and even then often only over a limited range of internuclear distance.

The ETDM for a particular transition may be found from experiment by the optimized fitting of simulated to measured spectra.<sup>1</sup> However, due to often limited discharge conditions only a small proportion of the band system is observed. Thus the ETDM is often only recovered for a small range of internuclear separation. On the other hand, the entire ETDM can be found by calculating it *ab initio*, which is however an involved and specialized task. As such, possessing the means to reliably estimate the ETDM before recourse to theoretical or experimental measures can be of great use.

We are currently studying the high pressure sulfur lamp numerically as well as from an experimental point of view.<sup>2,3</sup> The system is an efficient visible light radiator and produces a seemingly continuous spectrum from 300 to 900 nm. In short, the spectrum can be attributed to radiative transitions between all vibrational levels in the BX system of the sulfur dimer. Thus quanta are produced over the complete range of internuclear distance. This is a situation where full knowledge of the ETDM is required and a rare one where the data are in fact available.<sup>4</sup> However, two other group VI elements, selenium and tellurium, display similar high pressure spectra to the sulfur, also attributable to BX radiation, and we expect to verify and perhaps enhance our understanding of the sulfur lamp by studying these systems. For these dimers ETDM data have only recently appeared in the literature and indeed

only over a limited range of separation, centered around the equilibrium separation. So here is a specific case where the full ETDM is needed to describe the physical behavior of a system but where it is lacking and a semiempirical approach would be valuable.

To this end we have sought and found two such approaches in the literature. First, there is the direct approach of Woerdman<sup>5</sup> in which the ETDM is determined as a function of internuclear distance using the transition frequency to provide its shape. Furthermore, asymptotic correctness is ensured by establishing the magnitude of the molecular oscillator strength in terms of that of the associated atomic absorption as  $r \rightarrow \infty$ . A second method, inferred from the work of Monyakin,<sup>6,7</sup> uses the ETDM of a reference transition in one molecule to find that in an isovalent species, that one with the same number of valence electrons. Here, a radial scaling is performed to allow the mapping between different sized molecules. The former approach is not applicable to asymptotically forbidden transitions while there is no particular objection to this in the Monyakin method. Since the atomic absorptions associated with the transitions in the group VI dimers in which we are interested are forbidden, our goal is to find a rule to allow the ETDM for such transitions to be calculated.

The article is laid out as follows: We first introduce relevant terms and examine the two empirical approaches. After discussing their efficacy we propose a new scaling rule which uses a reference ETDM to determine that for an identical transition in an isovalent molecule, much like Monyakin's method but which also ensures asymptotic correctness, the importance of which we learned from Woerdman's approach. We provide an appropriate radial scaling factor and propose a rule applicable to asymptotically forbidden transitions. The rules are tested by finding the AX and BX ETDMs in  $\text{Na}_2$  from those in  $\text{Li}_2$ , which are asymptotically allowed, and the ETDM for the BX transitions in  $\text{O}_2$ ,  $\text{Se}_2$ , and  $\text{Te}_2$ , which are asymptotically forbidden, are found from that in  $\text{S}_2$ . Finally, we finish with our conclusions.

<sup>a)</sup>Electronic mail: J.J.A.M.v.d.Mullen@tue.nl

## II. EMPIRICAL METHODS

As opposed to atomic spectroscopy where the oscillator strength plays a large role, it is the ETDM that is significant in molecular spectroscopy. That this is the case is due to the spatial extent of an electronic state in a molecule which would require the oscillator strength and hence dipole polarizability to be determined as a function of frequency. The ETDM for a transition between two electronic states,  $A$  and  $B$ , is defined as follows:

$$M(r) = \left\langle \psi_A \left| \sum e \mathbf{r}_i \right| \psi_B \right\rangle, \quad (1)$$

where  $r$  is the internuclear distance,  $\psi_A$  and  $\psi_B$  are the electronic wave functions, and the moment operator sum extends over all electrons, with the electron position vector given by  $\mathbf{r}$ .

*Direct approach.* The oscillator strength for a given transition in a molecule is given in terms of the ETDM,  $M(r)$ ,

$$f(r) = \frac{g_A}{g_B} \frac{8\pi^2 m_e \nu(r)}{3he^2} M(r)^2,$$

where  $m_e$  is the electron mass,  $\nu(r)$  is the frequency of the transition, and the statistical weights for the upper and lower states are given by  $g_A$  and  $g_B$ , respectively. What Woerdman did was to turn this expression around so that the ETDM depends on the oscillator strength

$$M(r) = \left( \frac{3he^2}{8\pi^2 m_e \nu_{AB}(r)} \frac{g_B}{g_A} f(r) \right)^{1/2}. \quad (2)$$

Since everything is known once we are in possession of the state potential energy curves the problem becomes one of finding the oscillator strength. If a semiempirical way can be found to estimate it, the problem is solved. In considering the  $X^1\Sigma_g^+ \rightarrow A^1\Sigma_u^+$  and the  $X^1\Sigma_g^+ \rightarrow B^1\Pi_u$  absorptions in the lithium and sodium dimers, Woerdman estimated the asymptotic magnitude of the molecular oscillator strength for these transitions by ensuring asymptotic correctness. The potentials for the states considered are shown in Fig. 1 and as can be seen, both the  $A$  and  $B$  states share the same asymptote. Woerdman proposed that since either the  $B$  or  $A$  state could be responsible for the transition at  $r \rightarrow \infty$ , the sum of the molecular oscillator strengths is twice that of the atomic transition

$$f_{X \rightarrow B} + f_{X \rightarrow A} = 2F,$$

where  $F$  is the atomic value. Furthermore, he states that as  $r \rightarrow \infty$  the molecular wave functions are essentially atomic so that the ETDMs should be equal. If that is the case, then the ratio of the molecular oscillator strengths is given by that of the statistical weights of the upper levels, so that

$$f_{X \rightarrow B} / f_{X \rightarrow A} = g_B / g_A = 2,$$

where  $g_A = 1$  and  $g_B = 2$ . Thus, for the aforementioned absorptions the asymptotic values of the molecular oscillator strengths are

$$f_{X \rightarrow B} = 4/3F,$$

$$f_{X \rightarrow A} = 2/3F.$$

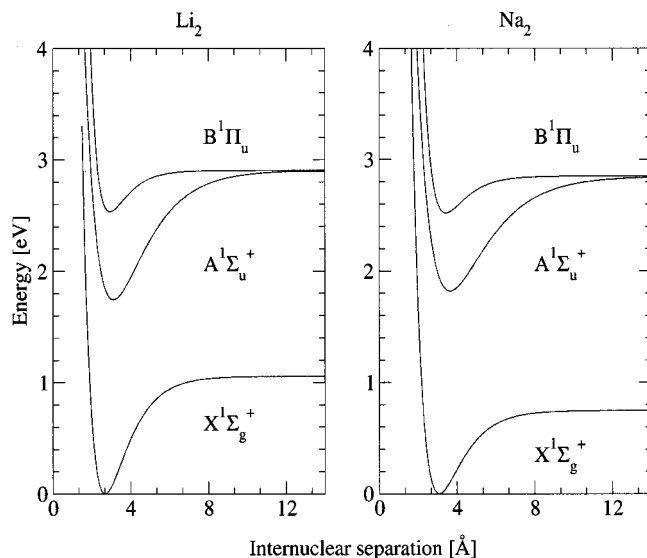


FIG. 1. Potential energy curves for the  $B^1\Pi_u$ ,  $A^1\Sigma_u^+$ , and  $X^1\Sigma_g^+$  states in  $\text{Li}_2$  and  $\text{Na}_2$ .

The results of using these values in Eq. (2) for  $\text{Li}_2$  are shown in Fig. 2(a) along with the literature data for the ETDMs. For both transitions the ETDMs found with Eq. (2) are within 8% of the reference values but for  $\text{Na}_2$  Woerdman reports errors up to 30%. The principle reason for the success of this approach is the fact that if the oscillator strength is constant then Eq. (2) demands that  $M(r)^2 \times \nu(r)$  is also a constant—a property that the alkali dimers do display. This means that the radial shape of the ETDM is determined solely by the transition frequency. In Fig. 2(b) we show the ETDM for the AX transition in  $\text{Li}_2$  along with the transition frequency. It is immediately clear that the position of the maximum in the ETDM lies at the same position as the minimum in the frequency and we can rely on it to provide the correct shape of the ETDM.<sup>8</sup>

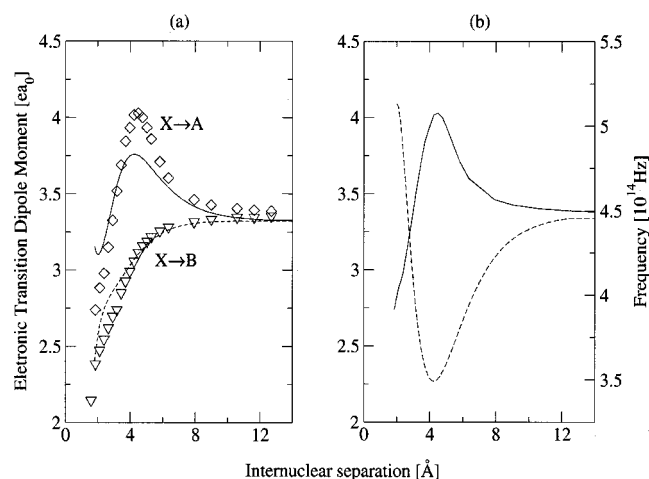


FIG. 2. On the left the reference data (Ref. 9) ETDMs for the AX and BX transitions in  $\text{Li}_2$  are shown (symbols) along with the results of Woerdman's approach (lines). On the right we show the ETDM for the AX transition along with the frequency as determined from the state potentials shown in Fig. 1. It is immediately apparent that the shape of the transition frequency can be found back in the ETDM.

This approach cannot be used for asymptotically forbidden transitions since there is no way we can relate oscillator strength behavior inside a molecule that radiates to that in the corresponding atom state that does not. Furthermore, the method has been criticized<sup>9</sup> as not being able to reproduce the local minima and maxima that can be found in the ETDMs of alkali dimers.

### III. SCALING APPROACH

Another method can be drawn from the work of Monyakin. After observing some regularities in the ETDMs of tin halides he proposed a scaling rule, where the ETDM in one species is determined from that in another. The rule for isovalent molecules is

$$M^A(r_{00}^A) = M^B(r_{00}^B) \left( \frac{\omega_e^B}{\omega_e^A} \right)^{1/2}, \quad (3)$$

where  $A$  and  $B$  denote the desired and reference transitions,  $\omega_e$  is the vibrational spectroscopic constant for the lower electronic state in the transition, and  $r_{00}$  is the  $r$ -centroid for the (0,0) vibrational transition. The latter is the mean radius at which a vibrational transition takes place and is defined as

$$r_{v'v''} = \frac{\langle \psi_{v'} | r | \psi_{v''} \rangle}{\langle \psi_{v'} | \psi_{v''} \rangle}, \quad (4)$$

where  $\psi$  is the vibrational wave function. The rule has been tested extensively but proves too unreliable. Since neither information about the upper state in the transition nor the frequency appear in Eq. (3) its accuracy will be and indeed is hit and miss. Furthermore, it provides the ETDM at one radial position only. Nevertheless, we see how a radius scaling can be achieved via the  $r$ -centroid.

### IV. ASYMPTOTICALLY CORRECT SCALING RULE

Our stated goal is to arrive at rules for the ETDM that are applicable to asymptotically allowed as well as forbidden transitions. Given the preceding approaches we can follow two paths—the direct or scaling one. The main problem, as mentioned before, with a direct approach is that it is unclear how to proceed when the associated atomic transition is forbidden. We can illustrate this by examining the BX transition in the sulfur dimer. In Fig. 3 we show state potentials and the ETDM for the transition<sup>4</sup> along with the frequency as a function of internuclear distance. The ETDM rises at first from 1 to 2 Å but with larger separations it falls to zero. In contrast to the situation in  $\text{Li}_2$ , the frequency does not reflect the radial behavior of the moment. It could be argued that up to 2 Å a direct approach may work, but beyond this the ETDM falls while  $1/\nu(r)$  rises to reach a plateau at large separations. The trick then would seem to be to find means of interpolating the ETDM from the maximum to large values of  $r$ . Even so we are not certain to be able to identify the maximum, if indeed there is one, from the frequency data. Thus, a direct approach seems unlikely to be fruitful.

In light of this we are forced to choose a scaling approach, which can have distinct advantages. It has been argued before that since the electron distributions in bound

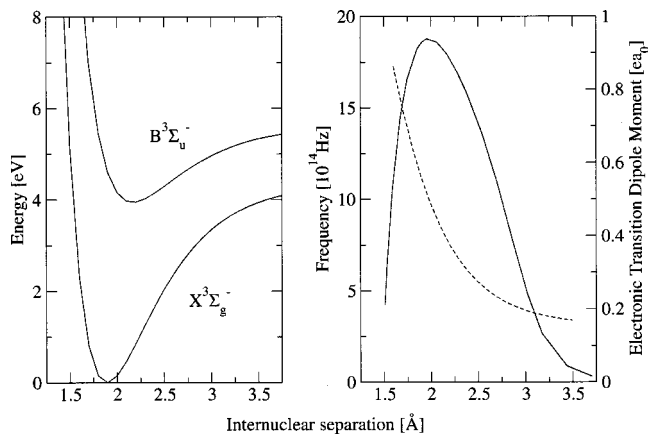


FIG. 3. On the left we plot the potential energy curves for the  $B$  and  $X$  states in the sulfur dimer. On the right we show the ETDM (solid line) and the transition frequency (dashed line). Here we see that the shape of the dipole is little related to that of the transition frequency.

atoms are highly localized, it is the valence or bonding electrons that dominate the dipole moment operator. If this is the case, then diatomic species with the same number of valence electrons will have similar moment operators, scaled only for the size difference between systems. Here, a scaling approach, using a reference ETDM from an isovalent molecule to that in one in which we are interested may be successful if we can find a suitable radial and magnitude scaling factors. The idea being that if the reference ETDM falls to zero with increasing internuclear separation, we are sure that the desired moment will do the same.

#### A. Asymptotically allowed transitions

We will first test this hypothesis by constructing a rule for allowed transitions and test it on  $\text{Li}_2$  and  $\text{Na}_2$ . Taking the ratio of two ETDMs for a desired transition  $A$  and a reference one  $B$ , we have from Eq. (2)

$$\frac{M^A(r)}{M^B(r')} = \left( \frac{\nu^B(r') f^A}{\nu^A(r) f^B} \right)^{1/2}, \quad (5)$$

where the statistical weights of the upper states in the transition are equal and  $r' = g(r)$ , a radial scaling function which we have yet to define. Thus, the magnitude of the reference ETDM is modified by the ratio of the frequencies and oscillator strengths and the radial extent is shifted by the function  $g(r)$ . What this might be follows from Monyakin—using the  $r$ -centroid allows a correct comparison between equivalent vibrational transitions and hence radii. Nevertheless, one cannot simply map the  $r$ -centroid for each transition from one system to another as it is highly unlikely that both will have the same number of vibrational levels. Furthermore, the effort in calculating a somewhat substantial mapping cannot be justified by the simplicity of Eq. (5). Thus, we choose the simplest mapping possible—between the (0,0) transitions. Thus we find that

$$r' = r \times \frac{r_{00}^B}{r_{00}^A}, \quad (6)$$

TABLE I.  $r$ -centroids for the test species.

Molecule	Transition	$r_{00}$ (Å)
Li <sub>2</sub>	$A^1\Sigma \rightarrow X^1\Sigma$	2.891
Na <sub>2</sub>	$A^1\Sigma \rightarrow X^1\Sigma$	3.354
O <sub>2</sub>	$B^3\Sigma \rightarrow X^3\Sigma$	1.387
S <sub>2</sub>	$B^3\Sigma \rightarrow X^3\Sigma$	2.016
Se <sub>2</sub>	$B^3\Sigma \rightarrow X^3\Sigma$	2.304
Te <sub>2</sub>	$B^3\Sigma \rightarrow X^3\Sigma$	2.678

which is intuitively correct. If the reference molecule  $B$  is larger than the desired molecule  $A$ , then the ratio of the  $r$ -centroids ensures that the reference ETDM is compressed, and vice-versa. The final problem is that of the oscillator strengths. Since there is already long-range information present in the reference ETDM, simply using the atomic oscillator strength values seems reasonable. Thus we arrive at the following rule for asymptotically allowed transitions:

$$M^A(r) = M^B(r') \left( \frac{\nu^B(r) F_A}{\nu^A(r') F_B} \right)^{1/2}. \quad (7)$$

The frequency for each transition is determined from the vertical energy gap between the states.

**Validation.** To test this rule we will determine the ETDM for the  $A^1\Sigma \rightarrow X^1\Sigma$  and  $X^1\Sigma \rightarrow B^1\Pi$  transitions in Na<sub>2</sub> from those in Li<sub>2</sub>. The dipole moments for both are available in the literature<sup>9</sup> and the radial frequencies are found from the state potentials which we generate using Jhungs universal approach.<sup>10</sup> The atomic oscillator strengths are 0.753 for lithium<sup>11</sup> and 0.982 for sodium.<sup>12</sup> In order to calculate the  $r$ -centroid we use the SCHROED program,<sup>13</sup> which provides the wave functions and employ the integration routines provided by the GNU Scientific Library (GSL). The values can be found in Table I. (A quicker way to find the zeroth  $r$ -centroid is to find the halfway point between the equilibrium distances of the two states. This is just as accurate as using Eq. (4)).

The results of applying the new rule for finding the sodium moments are shown in Fig. 4. The difference between the literature values and derived ones is less than 10%, more accurate than Woerdman's approach, and the asymptotes are well described, although there is a slight shift in the peak position.<sup>14</sup>

## B. Asymptotically forbidden transitions

The situation here is less straightforward. There is little we can do to anticipate, in general, what happens inside the molecule when the atomic state does not radiate. Nonetheless, we can rely on the reference ETDM to fall to zero and allow the atomic oscillator strengths to be equal. The radial scaling takes place as before, though now the transition frequencies are solely responsible for the magnitude scaling. Thus the rule for forbidden transitions becomes

$$M^A(r) = M^B(r') \left( \frac{\nu^B(r')}{\nu^A(r)} \right)^{1/2}. \quad (8)$$

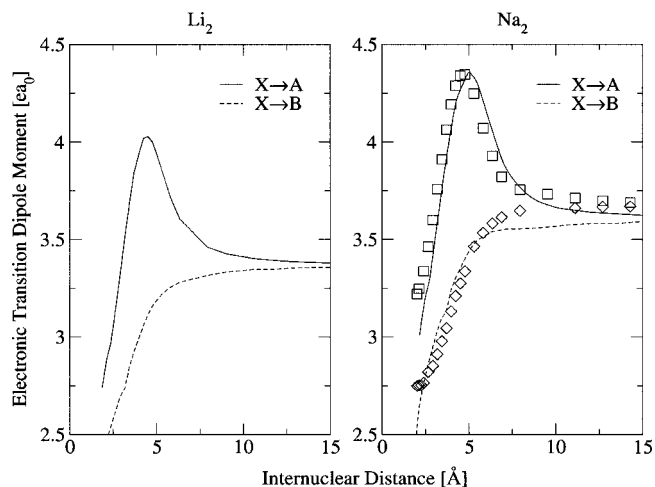


FIG. 4. On the left we show the literature ETDMs for the Li<sub>2</sub> transitions again, and on the right we show those for the sodium transitions (symbols). Also shown on the right are the ETDMs derived from the lithium data using Eq. (7). The very slight shift in the derived data and the large asymptotic values are most likely due to differing spectroscopic constants used in this work as compared to Ref. 9.

What these rules essentially say is that the atomic nature of the transition is carried into the molecule and the influence of this is expressed in the ratio of the oscillator strengths.

**Validation.** We now examine at the B→X in several group VI molecules to demonstrate this rule. The radial frequencies and  $r$ -centroids for these molecules were calculated as before and the latter can be found in Table I. In Fig. 5 we show the literature values of the transition moment for O<sub>2</sub>,<sup>15</sup> S<sub>2</sub>,<sup>16</sup> and Te<sub>2</sub>.<sup>17</sup> Also shown are the results of applying Eq. (8) to find the moments for O<sub>2</sub>, Se<sub>2</sub>, and Te<sub>2</sub> using the S<sub>2</sub> data<sup>4</sup> a reference. The data derived from the sulfur moment gives not only an extremely good value but the radial behavior is very well described. The largest error of 15% is found in the derived Se<sub>2</sub> data where it would seem that the radial scaling was not quite sufficient. Nevertheless, the radial shape is well described.

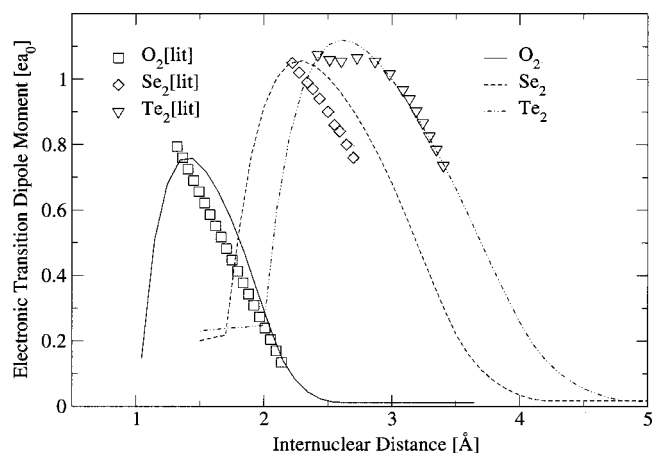


FIG. 5. Literature values for ETDMs for the BX transitions in O<sub>2</sub>, Se<sub>2</sub>, and Te<sub>2</sub> are shown (symbols) along with the values derived from the ETDM from the sulfur dimer, taken from Fig. 3, using Eq. (8).

## V. CONCLUSIONS

In this work we have critically reviewed two existing empirical techniques for the determination of the electronic transition dipole moment or ETDM in diatomic molecules. We have achieved our goal of establishing rules for determining the ETDM for an unknown transition. As a result of examining Woerdman's and Monyakin's work we have found that a direct approach, one where only information about the transition of interest is used, is unlikely to work unless one can relate the atomic oscillator strength to that inside the molecule, which is an unlikely prospect. Understanding the importance of establishing asymptotic correctness and recognizing the usefulness of the  $r$ -centroid approach as means to scale between systems, we have been able to propose new scaling rules for finding the ETDM. This method requires a reference ETDM for a transition in a molecule that is isoivalent to the desired one together with the transition frequency. There are two versions for the rule, one for asymptotically allowed and forbidden transitions. We have tested the former by finding ETDMs in  $\text{Na}_2$  for the AX and BX transitions from those in  $\text{Li}_2$ . The rule for asymptotically forbidden transitions was tested by finding the ETDM for the BX transitions in  $\text{O}_2$ ,  $\text{Se}_2$ , and  $\text{Te}_2$  from that in  $\text{S}_2$ . In all cases the derived values agreed within 15% of the literature values. The strength of the approach is that we use the reference ETDM to describe that in a species where it is unknown and use readily available data—the transition frequencies and atomic oscillator strengths to ensure that the magnitude is correct. Furthermore, the  $r$ -centroid scaling we

employ is readily performed. We find the accuracy of the new approach more than sufficient given its simplicity. Finally, extension of the rules to heteronuclear molecules should be possible.

- <sup>1</sup>M. E. Akopyan, M. K. Bibinov, D. B. Kokh, A. M. Pravilov, and M. B. Stepanov, *Chem. Phys.* **242**, 253 (1999).
- <sup>2</sup>C. W. Johnston, H. van der Heijden, G. M. Janssen, and J. J. A. M. van Dijk van der Mullen, *J. Phys. D* **35**, 342 (2002).
- <sup>3</sup>C. W. Johnston and J. J. A. M. van der Mullen (unpublished).
- <sup>4</sup>A. D. Pradhan and H. Partridge, *Chem. Phys. Lett.* **255**, 163 (1996).
- <sup>5</sup>J. P. Woerdman, *J. Chem. Phys.* **75**, 5577 (1981).
- <sup>6</sup>A. P. Monyakin *et al.*, *Opt. Spektrosk.* **48**, 11 (1980).
- <sup>7</sup>A. P. Monyakin *et al.*, *Opt. Spektrosk.* **48**, 243 (1980).
- <sup>8</sup>W. J. Stevens, M. M. Hessel, P. J. Bertocini, and A. C. Wahl, *J. Chem. Phys.* **466**, 1477 (1977).
- <sup>9</sup>D. D. Konowalow, M. E. Rosenkrantz, and D. S. Hochauer, *J. Mol. Spectrosc.* **99**, 321 (1983).
- <sup>10</sup>K. S. Jung, I. H. Kim, K. Oh, and K. B. Hahn, *Phys. Rev. A* **42**, 6497 (1990).
- <sup>11</sup>W. L. Wiese, M. W. Smith, and B. M. Miles, *Atomic Transition Probabilities*, Natl. Stand. Ref. Data Ser. Natl. Bur. Stad., Circ. 4 (US GPO, Washington, D.C., 1966), Vol. 1.
- <sup>12</sup>W. L. Wiese, M. W. Smith, and B. M. Miles, *Atomic Transition Probabilities*, Natl. Stand. Ref. Data Ser. Natl. Bur. Stad., Circ. 22 (US GPO, Washington, D.C., 1969), Vol. 2.
- <sup>13</sup>A. Pashov, W. Jastrzebski, and P. Kowalczyk, *Comput. Phys. Commun.* **128**, 622 (2000).
- <sup>14</sup><http://sources.redhat.com/gsl/>
- <sup>15</sup>B. R. Lewis and S. T. Gibson, *J. Chem. Phys.* **93**, 7532 (1990).
- <sup>16</sup>C. Heinemann, W. Koch, G. Linder, D. Reinen, and P. Widmark, *Phys. Rev. A* **54**, 1979 (1996).
- <sup>17</sup>A. Zaitsevskii, R. Ferber, and C. Teichtel, *Phys. Rev. A* **63**, 042511 (2001).