

Determination of Interatomic Potentials of He₂, Ne₂, Ar₂, and H₂ by Wave Function Imaging

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We report on a direct method to measure the interatomic potential energy curve of diatomic systems. A cold target recoil ion momentum spectroscopy reaction microscope was used to measure the squares of the vibrational wave functions of H₂, He₂, Ne₂, and Ar₂. The Schrödinger equation relates the curvature of the wave function to the potential $V(R)$ and therefore offers a simple but elegant way to extract the shape of the potential.

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Introduction.— Interaction potentials between the building blocks of matter shape the structure of bound species on a fundamental level. In the context of atomic and molecular physics potentials of interest are, e.g., the van der Waals potential or, within the Born-Oppenheimer approximation, the potential energy surfaces of molecules. For a given potential, the Schrödinger equation is typically considered as the condition equation for the wave function of a bound system. Mathematically, however, also the reverse is true: a given bound state wave function $\Psi(R)$ of a two-particle system determines the full functional dependence of the interaction potential $V(R)$ between the particles,

$$V(R) = \frac{\hbar^2}{2\mu} \frac{d^2\Psi(R)}{dR^2} + E. \quad (1)$$

Furthermore, the energy E of the bound state is also contained in the wave function, as the wave function's exponential decay for $R \rightarrow \infty$ is solely determined by the reduced mass μ of the system and E [1,2]. The wave function of a diatomic vibrational ground state is real valued. Therefore, such wave functions and their second derivative are experimentally accessible by measuring their density distribution. In molecular physics, today, state-of-the-art imaging techniques like Coulomb explosion imaging provide such density distributions and hence open the door to pursue this direct access to interaction potentials, as we will show in this Letter. We utilize the measured square of the wave function of the van der Waals-bound systems He₂, Ne₂, and Ar₂ as well as of the covalently bound H₂ in coordinate space to obtain the respective interaction potential $V(R)$ as a function of the internuclear distance R .

The traditional way of probing the potential between two particles is by performing elastic scattering experiments.

The integral and differential scattering cross sections rely on the exact shape of the internuclear potential, which therefore can be reconstructed by analyzing the measured deflection pattern. Interference patterns, originating from different trajectories leading to identical deflection angles having different phases, enable a precise determination of the attractive, the repulsive, and the well region of the potential $V(R)$. In order to extract the shape of $V(R)$ from such measurement, generally two approaches are possible. First, one can assume a theoretical potential function between two particles and calculate the resulting deflection pattern for a given relative particle speed. This theoretical pattern is compared to the measured one, and the parameters of the function are then varied until good agreement is reached [3,4]. Second, one can solve the inverse problem of scattering and infer the shape of the potential directly from the angular and energy dependence of the measured cross section [5,6].

Another approach for accurate determination of diatomic potentials is based on the rovibrational spectroscopy. For this, the measured transitions between rovibronic levels are fitted to the calculated ones based on the particular potential model.

Our alternative approach using Eq. (1) does not rely on scattering or spectroscopic transitions. While the accuracy of our method is not yet competitive to accuracies reached in the established techniques, it allows, in principle, for a direct access to the shape of the potential for the full range of internuclear distances R . No theoretical assumptions about the shape of the potential are required. Furthermore, the current approach allows for the most direct determination of the zero-point vibrational energy.

Experimental approach.—We measured the square of the ground state wave functions of the diatomic systems H₂, He₂, Ne₂, and Ar₂ employing Coulomb explosion imaging

using a cold target recoil ion momentum spectroscopy (COLTRIMS) setup [7–9]. In brief, a supersonic gas jet consisting of the target molecules or rare gas dimers is intersected with ionizing light from either a synchrotron or strong femtosecond laser. Charged fragments created in the photoreaction are then guided by a homogeneous electric field towards a time and position sensitive microchannel plate detector. By measuring the positions of impact and the times of flight of each charged particle, the particles’ initial vector momenta can be reconstructed yielding all derived quantities as kinetic energies or emission directions. All charged photofragments are measured in coincidence. The supersonic gas jet is created by expanding the target gas through a small aperture into a vacuum. For examining the rare gas dimers, additionally, a matter wave diffraction approach was employed as mass selector. While the expansion conditions were chosen such that considerable shares of helium, neon, or argon dimers, respectively, occurred in the supersonic jet, clusters of other sizes are created, as well. In order to select the dimers from the condensed gas beam, a 100 nm transmission grating has been installed in the path of the gas jet. The emerging diffraction separates particles in the gas jet according to their mass [10] towards slightly different deflection angles. The experiments were then performed by focusing the ionizing light into the part of the diffracted beam belonging to dimers.

By doubly ionizing the molecular system under investigation, two ions repelling each other by their Coulomb forces are created. In the subsequently occurring Coulomb explosion, the potential energy of the two ions (initially located at an internuclear distance R) converts into kinetic energy of the ions [kinetic energy release (KER)]. The KER is measured using the COLTRIMS reaction microscope and can be used to reconstruct the internuclear distance at the instant of the ionization via the so-called reflection approximation (in atomic units),

$$R = \frac{1}{\text{KER}}. \quad (2)$$

By recording a large number of Coulomb explosion events, we obtain the distribution of internuclear distances R occurring in the system. Accordingly, this distribution represents a direct measurement of the square of the vibrational wave function $|\Psi(R)|^2$.

Results and discussion.— H_2 : As a first example, we present our results on the hydrogen molecule. For this experiment, we used single photon double ionization by 160 eV photons provided by the advanced light source synchrotron in Berkeley (same experimental setup as in [11,12]). At this photon energy, one of the electrons absorbs the synchrotron light and the second electron is released via a shake- or knockoff processes [13]. As Coulomb explosion imaging relies on the R independence

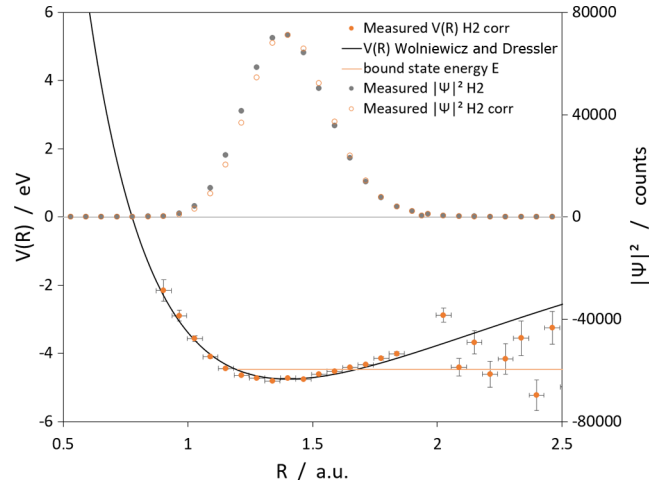


FIG. 1. Measured potential energy curve of H_2 . Experimental data (orange dots) are shown in comparison with a calculation by Wolniewicz and Dressler [17] (black line). Correcting the measured distance distribution (gray dots) according to the R dependence of the ionization probability results in the measured square of the wave function $|\Psi|^2$ (open dots).

of the ionization process, we corrected our measured KER distributions for known small R dependences of the respective double ionization process. The photoelectron emission from homonuclear diatomic molecules is strongly influenced by interference phenomena that appear due to the two-center nature of the molecule. This interference is known to modulate the photoabsorption cross section of the molecule [14,15] according to

$$\sigma \sim \sigma_H(Z^*) \left(1 + \frac{\sin(kR)}{kR} \right), \quad (3)$$

where σ_H is the atomic photoionization cross section for an effective charge Z^* and k is the electron wave vector. In single photon double ionization, as demonstrated in [12], a corresponding dependence is observable in the sum momentum of the two emitted electrons. The measured $|\Psi(R)|^2$ has been corrected correspondingly, applying a mean sum momentum k_{mean} of 2.9 a.u. Despite this inconvenience, single photon double ionization induced by soft x-ray synchrotron light is far superior to, e.g., laser-based sequential double ionization for triggering a Coulomb explosion, as it is instantaneous on the timescale relevant for nuclear motion. This is especially vital for light systems with steep potential energy surfaces of the intermediate singly charged ionic state, as for example, H_2^+ .

Figure 1 shows the results of our measurement and the application of Eq. (1) to the measured data in order to obtain $V(R)$. A binding energy $D_0 = 4.478$ eV [16] of the hydrogen molecule was assumed. After adjusting the measured KER values by 3%, which is within the estimated uncertainty of the KER calibration in this particular experiment, the measured potential shows excellent agreement

TABLE I. Parameters as obtained from the measured $V(R)$ distributions. The positions of the minima of the potentials R_e and the zero-point vibrational energies (ZPVE = $D_e + E$) are compared with reference values. The experimental error ranges give the 1σ confidence level of the fit e_{stat} plus the systematic error e_{sys} in parentheses (e_{stat}) (e_{sys}).

	$R_{e,\text{measured}}$ (a.u.)	$R_{e,\text{reference}}$ (a.u.)	$(D_e + E)_{\text{measured}}$ (meV)	$(D_e + E)_{\text{reference}}$ (meV)
H ₂	1.34(1)(8)	1.401 25(4) [27]	-328(17)(44)	-270.20(1) [28]
He ₂	5.7(1)(1)	5.6080(1) [29]	-0.925(35)(19)	-0.948(1) [30]
Ne ₂	5.77(1)(11)	5.847(2) [24]	-1.31(7)(20)	-1.56(2) [24]
Ar ₂	7.19(2)(13)	7.107(6) [31]	-1.66(26)(12)	-1.85(5) [23]

with the calculated potential energy curve [17]. Furthermore, the measured potential allows us, for example, to extract the depths of the potential D_e and the equilibrium distance R_e . Table I presents the values obtained by fitting a Morse function to the measured H₂ potential.

Van der Waals-bound systems: The van der Waals-bound systems have been investigated using sequential tunnel ionization induced by a strong ultrashort laser pulse (Ti:Sa laser, Dragon KMLabs, 780 nm, 40 fs) in order to initiate the Coulomb explosion. The singly charged dimer could potentially change its internuclear distance in the time between the two sequential ionizations steps. Classical nuclear dynamics simulations suggest that this is negligible on the present level of accuracy (see [18,19]). Also, in this case, we account for an R dependence of the ionization rate. The ionization probability of tunnel ionization depends on the effective principal quantum number n^* , which factors in the ionization potential I_p [20]. In the second ionization step, the intermediate system [e.g., (He⁺)He] is ionized by the laser. Here the ionization potential is increased by the kinetic energy released in the Coulomb explosion. Therefore, the principal quantum number is modified to

$$n^* = \frac{Z}{\sqrt{2(I_p + \text{KER})}} \quad (4)$$

in the second ionization step. The tunnel ionization rate

$$\omega_{ADK} = \sqrt{\frac{3Fn^{*3}}{\pi Z^3} \frac{FD^2}{8\pi Z}} \exp\left(-\frac{2Z^3}{3Fn^{*3}}\right) \quad (5)$$

depends on the electric field of the laser F and the charge of the remaining ion Z , with $D = (4eZ^3/Fn^{*4})^{n^*}$. Since the KER depends on the separation of the atoms at the instant of ionization [see Eq. (2)], the tunnel ionization probability ω_{ADK} shows a corresponding dependency. Therefore, the distribution of R obtained in the measurement is not equal to the square of the vibrational wave function of the system, but equals the square of the wave function multiplied by tunnel ionization probabilities according to Eq. (5). The influence of this dependency can be substantial, as Figs. 3 and 4 reveal. The peak intensity of the laser in the focus, which is needed when evaluating Eq. (5), was estimated

by inspecting the ratio of the single ionization of monomers to the double ionization of dimers, after considering the detector efficiency of 0.6 and the fraction of dimers in the supersonic gas jet (1% for Ne₂ and 5% for Ar₂). This results in a laser peak intensity of 2.3×10^{14} and 8.2×10^{13} W/cm² in the Ne₂ and Ar₂ experiments, respectively. For future experiments, the effective laser intensity could be measured with an accuracy of better than 2% using the procedure described in [21]. The measurement of He₂ was conducted at a higher laser intensity, saturating the helium single ionization probability. Accordingly, the dependence of Eq. (5) on the KER can be neglected in this case. The measurement of the KER requires a careful calibration of the COLTRIMS reaction microscope. This calibration was done by resolving vibrational features occurring in the double ionization of O₂ and comparing them to a measurement of Lundqvist *et al.* [22]. This results in a KER uncertainty of less than 1%.

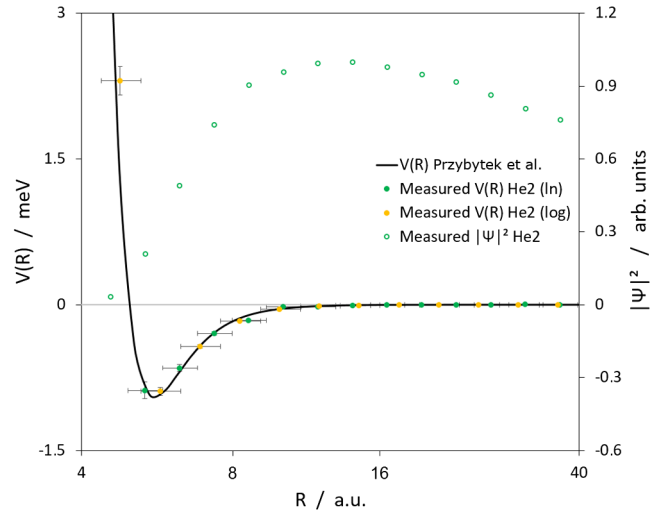


FIG. 2. Measured potential energy curve of He₂. Experimental data (dots) is shown in comparison with a calculation by Przybytek *et al.* [25] (black line). The measured square of the wave function $|\Psi|^2$ (open dots) is given on a logarithmic x scale (reanalyzed experimental data from the same experiment as in [1]). The green and yellow dots correspond to a binning on the basis of natural and decadic logarithms, respectively.

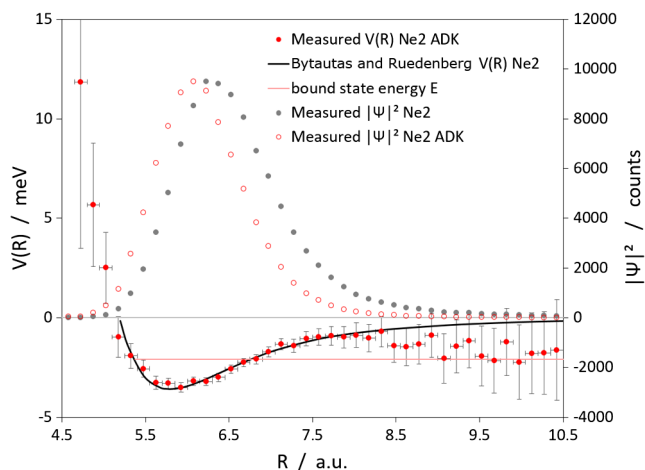


FIG. 3. Measured potential energy curve of Ne_2 . Experimental data (red dots) is shown in comparison with a calculation (black line) by Bytautas and Ruedenberg [26]. Correcting the measured distance distribution (gray dots) according to the R dependence of the ionization probability results in the measured square of the wave function $|\Psi|^2$ (open dots).

From the measured square of the wave function, we extracted the interaction potential $V(R)$ using Eq. (1). Obviously, this requires us to analyze the second derivative of the wave function Ψ , which needs to be computed numerically from the experimental data. This procedure is susceptible to statistical fluctuations, especially on the edges of the potential well where the wave function and thus our signal vanishes. To reduce this influence, the curvature was calculated including five adjacent data points instead of the minimal required three, in the case of the Ne_2 and Ar_2 measurements.

Figures 2–4 show our results for the squares of the wave functions and for the potentials of He_2 , Ne_2 , and Ar_2 , respectively. For Ar_2 , we used a binding energy of 10.5 meV [23], and for Ne_2 , we used a binding energy of 2.09 meV [24]. For He_2 , the binding energy of 0.15 μeV , obtained from the measured wave function itself [1], is negligible on the scale of the figure. The technique of extracting the binding energy is possible for any diatomic system, but relies on an exact measurement of the square of the wave function in the classically forbidden region, as explained in Ref. [1]. Therefore, in principle, the measurement of the potential $V(R)$ does not rely on the input of the binding energy.

The same quality of agreement between the predicted potential and our measurement as in the H_2 case is reached for He_2 comparing the experimental results to theoretical calculations by Przybytek *et al.* [25]. For the Ne_2 case, our measured potentials show excellent agreement with the calculations reported in [26]. We note that there are more than 3 orders of magnitude between the depth of the potentials of He_2 and H_2 , demonstrating the versatility of

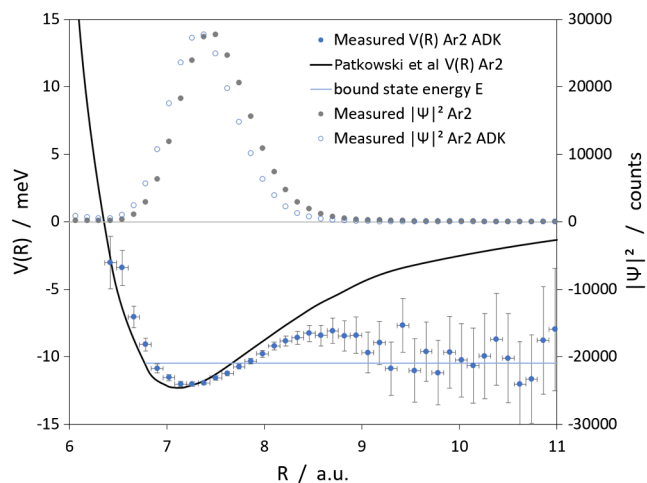


FIG. 4. Measured potential energy curve of Ar_2 . Experimental data (blue dots) is shown in comparison with a calculation (black line) by Patkowski *et al.* [23]. Correcting the measured distance distribution (gray dots) according to the R dependence of the ionization probability results in the measured square of the wave function $|\Psi|^2$ (open dots).

our approach. Only for Ar_2 does a deviation from the theoretically modeled curve [23] remain, even after correcting for the R dependence of the ionization probability. We attribute this to a systematical problem of this correction, as good agreement is obtained by assuming a lower ionization intensity (i.e., altering the ionization probabilities). For internuclear distances larger than 9 a.u., the measured potential energy curve of Ar_2 is lower than theory predicts. In fact, it converges to the value of the binding energy E . The reason for this is that the first term on the right-hand side of Eq. (1) converges to zero for larger interatomic distances in our analysis, but not to the theoretical value of $-E$. This shortcoming is most likely due to the low statistics of the measured square of the wave function at large interatomic distances, and therefore the proportionally stronger deviation due to background in the classically forbidden region. This effect can be seen in all cases, except He_2 , as the main part of this halo system lies in the tunneling region. To avoid that background, future work should aim for better vacuum ($< 2 \times 10^{-11}$ mbar). More efficient filtering of the background could be achieved by minimizing the recoil momentum of the electrons onto the center of mass of the two heavy fragments. This could be achieved by using free-electron laser radiation at an energy close to the ionization threshold (see [1]).

Table I summarizes the derived potential depths D_e and equilibrium internuclear distances R_e that result from fitting Lennard-Jones functions to the rare gas dimer potentials and compares them to experimental and theoretical reference values.

Conclusion.—We demonstrate the extraction of the interaction potential of diatomic systems from Coulomb explosion imaging data recorded by a COLTRIMS reaction

microscope. By employing an ionization process that is independent of the internuclear distance of the diatomic system, or which has a well-known dependency, the square of its wave function can be imaged. The wave function, along with the binding energy of the system, can subsequently be used for retrieval of the interaction potential $V(R)$ by inverting the Schrödinger equation. At the current state, the accuracy reached in our proof-of-concept experiments is competitive to other experimental techniques only for the case of He_2 . The promising route for improving on the experimental uncertainties is to use two photon double ionization at a FEL to ignite the Coulomb explosion. FELs have the advantage that, first, the KER calibration can be done *in situ* using O_2 [22] and, second, that corrections for an R dependence of the ionization probability become negligible. In addition, since the accuracy of the method depends on the accuracy of the wave function sampling, the longer acquisition times are desirable, in particular, for the regions where the wave function becomes small. The technique can be straightforwardly extended to molecular dimers as long as the internal potential energy scale of the molecular monomers is significantly different than the energy scale of the intermonomer interaction.

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- [1] S. Zeller *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **113**, 14651 (2016).
- [2] O. Kornilov and J. P. Toennies, *Europhysics News* **38**, 22 (2007).
- [3] J. M. Farrar and Y. T. Lee, *J. Chem. Phys.* **56**, 5801 (1972).
- [4] J. P. Toennies, *Faraday Discuss. Chem. Soc.* **55**, 129 (1973).
- [5] R. Feltgen, H. Pauly, F. Torello, and H. Vehmeyer, *Phys. Rev. Lett.* **30**, 820 (1973).
- [6] U. Buck, *Rev. Mod. Phys.* **46**, 369 (1974).
- [7] O. Jagutzki, A. Cerezo, A. Czasch, R. Dörner, M. Hattas, M. Huang, V. Mergel, U. Spillmann, K. Ullmann-Pfleger, T. Weber, H. Schmidt-Böcking, and G. D. W. Smith, *IEEE Trans. Nucl. Sci.* **49**, 2477 (2002).
- [8] J. Ullrich, R. Moshhammer, A. Dorn, R. Dörner, L. Ph. H. Schmidt, and H. Schmidt-Böcking, *Rep. Prog. Phys.* **66**, 1463 (2003).
- [9] T. Jahnke, Th. Weber, T. Osipov, A. L. Landers, O. Jagutzki, L. Ph. H. Schmidt, C. L. Cocke, M. H. Prior, H. Schmidt-Böcking, and R. Dörner, *J. Electron Spectrosc. Relat. Phenom.* **141**, 229 (2004).
- [10] W. Schöllkopf and J. P. Toennies, *Science* **266**, 1345 (1994).
- [11] D. Akoury *et al.*, *Science* **318**, 949 (2007).
- [12] K. Kreidi *et al.*, *Eur. Phys. J. Spec. Top.* **169**, 109 (2009).
- [13] A. Knapp, A. Kheifets, I. Bray, Th. Weber, A. L. Landers, S. Schössler, T. Jahnke, J. Nickles, S. Kammer, O. Jagutzki, L. Ph. Schmidt, T. Osipov, J. Rösch, M. H. Prior, H. Schmidt-Böcking, C. L. Cocke, and R. Dörner, *Phys. Rev. Lett.* **89**, 033004 (2002).
- [14] H. D. Cohen and U. Fano, *Phys. Rev.* **150**, 30 (1966).
- [15] S. E. Canton, E. Plésiat, J. D. Bozek, B. S. Rude, P. Decleva, and F. Martín, *Proc. Natl. Acad. Sci. U.S.A.* **108**, 7302 (2011).
- [16] K. Pachucki and J. Komasa, *J. Chem. Phys.* **144**, 164306 (2016).
- [17] L. Wolniewicz and K. Dressler, *J. Chem. Phys.* **82**, 3292 (1985).
- [18] M. Kunitski, S. Zeller, J. Voigtsberger, A. Kalinin, L. Ph. H. Schmidt, M. Schöffler, A. Czasch, W. Schöllkopf, R. E. Grisenti, T. Jahnke, D. Blume, and R. Dörner, *Science* **348**, 551 (2015).
- [19] J. Voigtsberger *et al.*, *Nat. Commun.* **5**, 5765 (2014).
- [20] M. V. Ammosov, N. B. Delone, and V. P. Krainov, *Zh. Eksp. Teor. Fiz.* **91**, 2008 (1986) [*Sov. Phys. JETP* **64**, 1191 (1986)].
- [21] W. C. Wallace, O. Ghafur, C. Khurmi, U. S. Sainadh, J. E. Calvert, D. E. Laban, M. G. Pullen, K. Bartschat, A. N. Grum-Grzhimailo, D. Wells, H. M. Quiney, X. M. Tong, I. V. Litvinyuk, R. T. Sang, and D. Kielpinski, *Phys. Rev. Lett.* **117**, 053001 (2016).
- [22] M. Lundqvist, D. Edvardsson, P. Baltzer, M. Larsson, and B. Wannberg, *J. Phys. B* **29**, 499 (1996).
- [23] K. Patkowski, G. Murdachaew, C.-M. Fou, and K. Szalewicz, *Mol. Phys.* **103**, 2031 (2005).
- [24] A. Wüest and F. Merkt, *J. Chem. Phys.* **118**, 8807 (2003).
- [25] M. Przybytek, W. Cencek, J. Komasa, G. Łach, B. Jeziorski, and K. Szalewicz, *Phys. Rev. Lett.* **104**, 183003 (2010).
- [26] L. Bytautas and K. Ruedenberg, *J. Chem. Phys.* **128**, 214308 (2008).
- [27] H. G. M. Edwards, D. W. Farwell, A. C. Gorvin, and D. A. Long, *J. Raman Spectrosc.* **17**, 129 (1986).

- [28] K. K. Irikura, *J. Phys. Chem. Ref. Data* **36**, 389 (2007).
[29] W. Cencek, M. Przybytek, J. Komasa, J. B. Mehl, B. Jeziorski, and K. Szalewicz, *J. Chem. Phys.* **136**, 224303 (2012).
[30] K. Patkowski, C. Wojciech, M. Jeziorska, B. Jeziorski, and K. Szalewicz, *J. Phys. Chem.* **111**, 7611 (2007).
[31] P. R. Herman, P. E. LaRoque, and B. P. Stoicheff, *J. Chem. Phys.* **89**, 4535 (1988).