Intermolecular interaction potentials for the Ar–C₂H₂, Kr–C₂H₂, and Xe–C₂H₂ weakly bound complexes: Information from molecular beam scattering, pressure broadening coefficients, and rovibrational spectroscopy

David Cappelletti

Dipartimento di Ingegneria Civile ed Ambientale, Università di Perugia, I-06100 Perugia, Italy

Massimiliano Bartolomei and Estela Carmona-Novillo

Instituto de Matemáticas y Física Fundamental, CSIC, E-28006 Madrid, Spain

Fernando Pirani

Dipartimento di Chimica, Università di Perugia, I-06100 Perugia, Italy

Ghislain Blanquet

Laboratoire de Spectroscopie Moléculaire, Facultés Universitaires Notre-Dame de la Paix, B-5000 Namur, Belgium

Franck Thibault

Laboratoire de Physique des Atomes Lasers Molécules et Surfaces (UMR-CNRS 6627), Université de Rennes I, Campus de Beaulieu, F-35042 Rennes Cedex, France

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Integral cross sections and pressure broadening coefficients have been measured for the acetylene-krypton complex, by molecular beam scattering and by high resolution IR spectroscopy, respectively. A new potential energy surface (PES) is proposed to describe structure and dynamical properties of this prototypical weakly bound complex. The PES has been parametrized exploiting a novel atom-bond pairwise additive scheme and has been fitted to the experimental data. A similar PES has been obtained for the acetylene-xenon system by a proper scaling of the interaction parameters of the krypton case, based on empirical considerations. These PESs together with that recently proposed by the same authors [J. Phys. Chem. **109**, 8471 (2005)] for the acetylene-argon case have been employed for close coupling calculations of the pressure broadening cross sections and for a characterization of the rovibrational structure of the complexes. © 2007 American Institute of Physics. [DOI: [10.1063/1.2434174](https://doi.org/10.1063/1.2434174)]

I. INTRODUCTION

Weakly bound complexes involving acetylene and rare gas atoms have been extensively investigated in recent years. As pointed out in most of the literature papers the interest for these systems stems from the presence of the triple carbon-carbon bond which makes acetylene a sort of prototype apolar anisotropic molecule and its complexes with rare gases worth to be studied.

The acetylene complexes with the lighter rare gases, He and Ne, due to their reduced size are somewhat more accessible to *ab initio* studies and already ten years ago realistic potential energy surfaces (PESs) have been calculated and tested on experimental data for He–C₂H₂ (Refs. 1 and 2) and Ne–C₂H₂.^{3,4} Specifically, the PESs of these weakly bound complexes show a very low anisotropy in the well region and the acetylene, in the complex, behaves as a free (He) or slightly hindered rotor (Ne). The measured near-infrared spectra of the complexes have been interpreted as spectra of the free acetylene molecule slightly perturbed by the rare gas atom.

The Ar–C₂H₂ system is by far the most studied case: High resolution spectroscopy data,^{5–10} molecular beam scat-

tering cross sections,^{11,12} and experimental pressure broadening coefficients^{13–16} are available in the literature. The opportunity of such an amount of experimental information has stimulated the production of a large number of PESs obtained either phenomenologically by fitting a selected set of experimental observables^{9,12,17,18} or from direct *ab initio* calculations at various level of sophistication.^{19–23} The anisotropy of the PES is stronger for the Ar case with respect to those shown by the lighter rare gas complexes, even if somewhat elusive.¹⁹ Anyway, the rotational spectrum of Ar–C₂H₂ is drastically different from that of Ne–C₂H₂,⁴ and despite the large amplitude internal motions of the system, it has been described with a semirigid rotor Hamiltonian.^{6,10}

Much less attention has been devoted to the heavier Kr and Xe complexes, for which only line shape and pressure broadening measurements have been published in the literature.^{15,24–26} No direct information are available on the PESs for these systems. Following the qualitative trend discussed above we expect the heavier complexes to be characterized by a strong interaction anisotropy and consequently by a much more rigid structure than those observed for the lighter rare gases.

We recently presented¹² an investigation of the

acetylene-argon PES by molecular beam scattering and pressure broadening experiments. Integral and differential cross sections, pressure broadening coefficients, and second virial coefficients were analyzed and a phenomenological PES was produced and shown to be consistent with all sets of experimental data. In order to complete the study of the Ar–C₂H₂ system we present here a calculation of its main spectroscopic features and compare them with data available in literature. More importantly, in this work we extend the research to the acetylene-krypton and acetylene-xenon complexes.

For the Kr–C₂H₂ system integral scattering cross sections have been measured, for the first time, by molecular beam technique. For the same system, pressure broadening coefficients have also been measured at two different temperatures, improving significantly previous measurements. In order to analyze the experimental data, a potential energy surface has been generated, exploiting the same atom-bond parametrization of the interaction energy²⁷ already adopted for the Ar case, and using the same methodology for the analysis of the data.

Finally, for the Xe–C₂H₂ case the PES has been directly generated, scaling some of the potential parameters of Kr–C₂H₂, on the basis of empirical considerations.^{28,29} Pressure broadening calculations have been performed with this new PES and the results have been compared with available experimental results.

The next section is devoted to the representation of the PES. Details of the experiments and data analysis are summarized in Secs. III–V. Bound states and spectral feature calculations are discussed in Sec. VI. The discussion and some final remarks will follow in Secs. VII and VIII, respectively.

II. REPRESENTATION OF THE POTENTIAL ENERGY SURFACE

The analytical representation of the potential energy surface is of the atom-bond pairwise additive type, as recently introduced by some of the authors.²⁷ Specifically, the interaction energy of a rare gas atom with the acetylene molecule has been represented as the sum of three atom-bond interaction pairs V_{ab} ,

$$V(R, \theta) = \sum_b V_{ab},$$

where R is the distance between the rare gas atom to the center of mass of the acetylene molecule, θ is the relative Jacobi angle, and b are the bonds of the acetylene molecule.

The parametrization adopted for the V_{ab} pair potentials is of the following type:²⁷

$$V_{ab}(r, \alpha) = \varepsilon(\alpha) \left[\frac{6}{n(r, \alpha) - 6} \left(\frac{r_m(\alpha)}{r} \right)^{n(r, \alpha)} - \frac{n(r, \alpha)}{n(r, \alpha) - 6} \left(\frac{r_m(\alpha)}{r} \right)^6 \right]. \quad (2.1)$$

In Eq. (2.1), r is the distance of the rare gas atom from the bond center and α is the angle that $\mathbf{r}$ forms with the bond axis considered; ε and r_m are the atom-bond interaction well

depth and its location, respectively. The n parameter is expressed as a function of both r and α using the following equation:²⁷

$$n(r, \alpha) = 9 + 4.0 \left(\frac{r}{r_m(\alpha)} \right)^2. \quad (2.2)$$

The dependence of ε and r_m from α is given by the following relationships:

$$\varepsilon(\alpha) = \varepsilon_{\perp} \sin^2(\alpha) + \varepsilon_{\parallel} \cos^2(\alpha), \quad (2.3)$$

$$r_m(\alpha) = r_{m\perp} \sin^2(\alpha) + r_{m\parallel} \cos^2(\alpha), \quad (2.4)$$

where $\varepsilon_{\perp}$, $\varepsilon_{\parallel}$, $r_{m\perp}$, and $r_{m\parallel}$ are, respectively, the well depth and equilibrium distance for the perpendicular and parallel approaches of the rare gas atom to the bond.

This approach treats the interaction as determined by a repulsion due to an effective size of the molecule²⁹ and an attraction arising from different dispersion centers distributed on the molecule. Such a formulation provides a realistic picture of both the repulsive and the attractive components of the interaction including, as effective contributions, three body²⁷ and other nonadditive terms. The CH bonds are assumed to have electronic charge distributions of near cylindrical symmetry. Therefore, in each atom-bond pair the dispersion center is set to coincide with the geometric bond center.

The parameters of the CH bond-rare gas interaction pairs have been determined recently on CH₄-rare gas and C₆H₆-rare gas complexes.²⁷ The performances of these PESs have been also evaluated by calculating static and dynamic properties of atom (and ion) clusters with hydrocarbon molecules.³⁰ These parameters are considered here fixed.

The parameters of the CC triple bond-Ar complex are those already published in Ref. 12. Values for the CC triple bond-Kr term have been obtained by using a semiempirical method,²⁹ employing as input data the CC triple bond polarizability tensor components, bond length, and the rare gas atomic polarizability. These initial values have been slightly refined during the fit of the experimental data varying them within the known uncertainties, as detailed in the Discussion. The parameters of the CC triple bond-Xe pair have been obtained from those of Kr by scaling the latter's on the basis of known empirical correlation formulas^{28,29} which take into account bond polarizabilities and the ratio between atomic polarizabilities of Kr and Xe.

All the parameter values necessary to represent the PESs of the Ar, Kr, and Xe acetylene complexes are given in Table I.

III. EXPERIMENTAL SECTION

A. Integral cross section measurements

The molecular beam apparatus employed for scattering cross sections measurements of the acetylene-Kr system is the same employed previously for the acetylene-Ar case¹² and has been described in details elsewhere.^{31,32} Total (elastic plus inelastic) integral cross sections $Q(v)$ have been measured in the velocity range of $0.6 \leq v \leq 2.0$ km/s. The experimental values of $Q(v)$ are reported in Fig. 1 as a func-

TABLE I. Potential parameters for the carbon-carbon triple bond (CC_{tr})-rare gas and CH-rare gas pairs. The perpendicular and parallel components of R_m and ϵ are in Å and in meV, respectively.

Pair	$R_{m\perp}$	$R_{m\parallel}$	$\epsilon_{\perp}$	$\epsilon_{\parallel}$
CC _{tr} -Ar ^a	3.960	4.200	9.800	10.400
CH-Ar ^b	3.641	3.851	4.814	3.981
CC _{tr} -Kr	4.080	4.291	11.000	13.600
CH-Kr ^b	3.782	3.987	5.667	4.781
CC _{tr} -Xe	4.209	4.426	13.000	16.250
CH-Xe ^b	3.976	4.175	6.233	5.384

^aFrom Ref. 12.

^bFrom Ref. 27.

tion of the acetylene beam velocity v and have been plotted as $Q(v)v^{2/5}$, as usual to emphasize the glory structure.

The experimental methodology and the settings of the apparatus will not be reported here because they are the same as in the case of the acetylene-Ar case and can be found in detail in Ref. 12. However, it is worth to remember that the molecular beam source has been heated at $T \sim 500$ K in order to boost the rotational temperature of the acetylene molecules. In these conditions the scattering experiment probes essentially the spherical averaged potential acting between the projectile molecules and the target atoms. As done previously for Ar,¹² the absolute values of total cross sections have been obtained by an internal calibration procedure.^{33,34}

B. Line profile measurements

For the mixture C₂H₂ diluted in Kr, the measurements were performed with an improved Laser Analytics (LS3

FIG. 1. Upper panel: Experimental total cross sections $Q(v)$ for scattering of rotationally "hot" acetylene near effusive beams by krypton, plotted as $Q(v) \times v^{2/5}$ (see text), as a function of the beam velocity v . The continuous line represents calculations with the present PESs. Lower panel: Calculated cross section for the spherical average interaction and for the low helicity (LH) and high helicity (HH) dynamical regimes (see text).

FIG. 2. Experimental and calculated pressure broadening (PB) coefficients for the Kr-C₂H₂ system. Solid lines: present CC/CS calculations; white circles: present experimental results at 297 K; white triangles: present experimental results at 173 K; black squares: results at 297 K (Ref. 15); black circles: results at 297 K (Ref. 24).

model) tunable diode-laser spectrometer. This apparatus and the absorption cells used at room and low (173 K) temperatures are described in detail elsewhere.^{35,36} The essential characteristics of the experiment are the following. At room temperature, 15 lines ranging between $P(2)$ and $R(26)$ have been studied in the $\nu_4 + \nu_5$ band; the path length was 4.17 m and the pressure of acetylene varied between 0.01 and 0.15 mbar following the line under study. At 173 K, 14 lines were recorded; the path length was 0.4043 m and the C₂H₂ pressure comprised between 0.08 and 0.80 mbar. For each line, four pressure values of Kr were used in the range of 30–75 mbars. For the data reduction, we used the same procedure as in Ref. 16. In each case, we have fitted the experimental measurements with both the Voigt and Rautian theoretical profiles. The errors reported in the tables are twice the standard deviation plus 2% to take into account various errors (pressure and temperature). Experimental results are plotted in Fig. 2 together with data from previous measurements and calculations, to be commented further on.

IV. COLLISION CROSS SECTION CALCULATIONS AND DATA ANALYSIS

The integral scattering cross sections of a highly rotationally excited molecule by a rare gas atom target is governed essentially by a central force field and is dominated by the elastic contribution, as extensively demonstrated in the past.^{37,38} In this situation some useful approximations can be safely introduced in the theoretical description of the collisions without losing any content of information on the interaction potential.

Herein, the collision dynamics has been modeled according to two different limiting regimes: a spherical model, where a central field scattering is operative and a molecular model, where the cross sections are determined by a combination of two partial orientationally averaged contributions.

The two regimes selectively emerge as a function of the ratio between the rotational time t_{av} ($\sim 4 \times 10^{-13}$ s, at $T_{\text{rot}} \sim 500$ K), required to induce an average of the interaction between limiting configurations of the complex, and the average collision time t_{coll} , which varies with the beam velocity.³² The estimated times indicate that at low collisional velocities, $t_{\text{coll}} \gg t_{\text{av}}$, rotationally excited acetylene molecules rotate sufficiently fast during a collision to be considered as spherical particles. In such conditions, collisions are mainly elastic and are driven by the spherical component of the interaction $\bar{V}(R)$, which can be obtained by averaging the PES over the θ angle,

$$\bar{V}(R) = \int_0^{\pi/2} V(R, \theta) \sin \theta d\theta. \quad (4.1)$$

At higher velocities $t_{\text{coll}} \sim t_{\text{av}}$ and the “molecular” collisional regime sets in. Here the appropriate dynamical model is characterized by partial averages over the helicity states, defined by the helicity quantum number M (the projection of the rotational angular momentum $\mathbf{j}$ along the collisional axis). In such conditions one can assume that collisions are driven by two effective potentials V_{LH} and V_{HH} which represent partial averages over the low helicity (LH) and high helicity (HH) states, respectively.

Specifically,

$$V_{\text{LH}}(R) = 2 \int_0^{\pi/3} V(R, \theta) \sin \theta d\theta \quad (4.2)$$

governs the collisions occurring essentially at small θ angles (which correlate with low helicity states), while

$$V_{\text{HH}}(R) = 2 \int_{\pi/3}^{\pi/2} V(R, \theta) \sin \theta d\theta \quad (4.3)$$

controls the collisions basically occurring at large θ angles (which correlate with high helicity states).

These partially averaged interactions satisfy the necessary condition that the spherical average of the interaction can be obtained by the averaged sum of V_{LH} and V_{HH} ,

$$\bar{V}(R) = \frac{V_{\text{LH}}(R) + V_{\text{HH}}(R)}{2}. \quad (4.4)$$

The main features of the $\bar{V}$, V_{LH} , and V_{HH} potentials for the intermolecular complexes studied in this work are reported in Table II.

The final calculated total cross sections have been obtained within the spherical model for $v \leq 0.6$ km/s and according to the molecular model for $v \geq 1.0$ km/s. In the latter case the calculated $Q_{\text{LH}}(v)$ and $Q_{\text{HH}}(v)$ cross sections, corresponding to the collisions driven, respectively, by $V_{\text{LH}}(R)$ and $V_{\text{HH}}(R)$ interactions, have been then combined as

$$\frac{Q_{\text{LH}}(v) + Q_{\text{HH}}(v)}{2}. \quad (4.5)$$

The switch between the two dynamical regimes at intermediate v has been carried out by a weighted sum (the weights depending on the velocity³²) of cross sections calculated for the two limiting cases.

TABLE II. Interaction energy D_e (meV) and equilibrium distance R_e (Å) for the spherical average interaction and limiting parallel and perpendicular geometries and low helicity (LH) and high helicity (HH) effective potentials of the acetylene-Ar, -Kr, and -Xe complexes.

System	R_e	D_e
C₂H₂-Ar		
$\bar{V}$	4.31	12.4
$V_{\perp}$	3.85	17.0
$V_{\parallel}$	4.79	10.7
V_{LH}	4.45	12.3
V_{HH}	3.91	16.8
C₂H₂-Kr		
$\bar{V}$	4.43	14.9
$V_{\perp}$	3.96	19.9
$V_{\parallel}$	4.91	13.5
V_{LH}	4.57	15.0
V_{HH}	4.03	19.7
C₂H₂-Xe		
$\bar{V}$	4.58	17.3
$V_{\perp}$	4.10	23.5
$V_{\parallel}$	5.08	15.6
V_{LH}	4.73	17.4
V_{HH}	4.17	23.0

The scattering cross sections have been calculated in the center of mass systems. Standard numerical techniques have been used for the phase shift evaluation.³⁹ The cross sections have been then convoluted in the laboratory frame and compared with the experimental data. A trial and error procedure allowed a fine tuning of some interaction potential parameters, namely, those related to the CC triple bond-Kr interaction term, in the atom-bond pairwise additive representation of the PES. The best fit final results are shown as continuous lines in the upper panel of Fig. 1. Q_{LH} , Q_{HH} , and the spherical cross sections are plotted in the lower panel of the same figure.

V. PRESSURE BROADENING CROSS SECTION CALCULATIONS

Within the impact approximation pressure broadening cross sections are provided by binary scattering $\mathbf{S}$ -matrix elements.^{40–42} Calculations were performed with MOLSCAT (Ref. 43) quantum dynamical scattering code. The coupled equations are solved by means of the hybrid log derivative–Airy propagator of Alexander and Manolopoulos.⁴⁴ The propagation is carried out with the log-derivative method from a minimum distance $R_{\text{min}} = 2.3$ Å to an intermediate distance $R_{\text{mid}} = 15$ Å, and then a switch to the Airy method is done up to a maximum intermolecular distance $R_{\text{max}} = 30$ Å. The interaction potential surfaces were projected over six Legendre polynomials $P_{\lambda}(\cos \theta)$. Recall that due to the homonuclear symmetry of acetylene only even values of λ are needed. The radial coefficients were obtained by a Gauss–Legendre quadrature over 20 points. Here, only half of these points are really needed. The total angular momentum $\mathbf{J} = \ell + \mathbf{j}$, where $\mathbf{j}$ is the rotational angular momentum, was held fixed to a maximum value of $J_{\text{max}} = 150$ to ensure the conver-

gence in partial waves (ℓ). As an example, for C₂H₂-Kr at a kinetic energy of 263 cm⁻¹ the convergence was reached for $J_{\max}=140$ (120) for the $R(0)$ ($R(20)$) pressure broadening cross sections. All energetically open rotational levels and at least four closed levels, two with odd and two with even rotational angular momentum value j , are included in the calculations for each total energy $E_T=E_{\text{kin}}+E_{\text{rot}}(j)$.

Since we compare our calculations with experimental pressure broadening coefficients for P or R lines we had to consider both species (*ortho* and *para*) of acetylene simultaneously even if they do not interconvert in our experiment. The rotational energy levels were generated with a fixed rotational constant ($B=1.176\,641$ cm⁻¹) and the same PES was considered in both ground and vibrationally excited states of C₂H₂. Indeed, the different PESs considered here do not include any vibrational dependence. In the rigid approximation we assume that the collisional width for a $R(j)$ line is equal to the width of the $P(j+1)$ line.⁴²

In the case of Kr as a perturber, the pressure broadening coefficients obtained for $R(j)$ lines, with j varying from 0 to 20, are the result of thermally averaged pressure broadening cross sections assuming a Maxwell-Boltzmann distribution for the thermal motion,

$$\gamma(j, T) = n_b \langle v \sigma_{\text{PB}}(j, E_{\text{kin}}) \rangle = n_b \bar{v} \bar{\sigma}_{\text{PB}}(j, T), \quad (5.1)$$

$$\bar{\sigma}_{\text{PB}}(j, T) = \left(\frac{1}{k_B T} \right)^2 \int_0^\infty E_{\text{kin}} \sigma_{\text{PB}}(j, E_{\text{kin}}) \times \exp(-E_{\text{kin}}/k_B T) dE_{\text{kin}}, \quad (5.2)$$

where n_b is the density of the perturbors, $\bar{v}=(8k_B T/\pi\mu)^{1/2}$ is the mean relative velocity for a sample at temperature T , and σ_{PB} stands for the real part of the generalized cross section $\sigma^{(1)}$ since we deal with IR lines.⁴²

Therefore, the normalized collisional half-width at half maximum (HWHM) γ_0 (in cm⁻¹ atm⁻¹ units) may be written as

$$\gamma_0 = \frac{\bar{v} \bar{\sigma}_{\text{PB}}}{2\pi c k_B T} = 56.6915 (\mu T)^{-1/2} \bar{\sigma}_{\text{PB}} \times 10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}, \quad (5.3)$$

where μ is the radiator-perturber reduced mass in amu and the cross section is in Å².

To this end the close coupling (CC) method (Ref. 45) was used to compute pressure broadening cross sections over a grid of kinetic energies (specifically, 10, 25, 50, 75, 100, 125, 153, 174, 220, 263, 320, and 400 cm⁻¹) and the less accurate, but less time consuming, coupled states (CSs) method⁴⁶⁻⁴⁸ was used for higher kinetic energies (i.e., 500, 750, and 1000 cm⁻¹). Note that $E_{\text{kin}}=\bar{E}_{\text{kin}}=(4k_B T)/\pi=153$ and 263 cm⁻¹ are the kinetic energies associated with the mean relative speed for the relevant experimentally studied temperatures $T=173$ and 297 K, respectively.

In Fig. 3 the variation of selected σ_{PB} as a function of this grid of energies is shown. Maxwell-Boltzmann distributions for $T=173$ and 297 K are also reported. Figure 4 compares thermally averaged γ_0 with unaveraged values as obtained from σ_{PB} calculated at $\bar{E}_{\text{kin}}$, by replacing in Eq. (5.3)

FIG. 3. Pressure broadening cross sections for selected transitions as a function of the collision energy, for the Kr-C₂H₂ system. Maxwell-Boltzmann distributions at the two experimentally investigated temperatures $T=173$ and 297 K are also shown. E_{kin}/hc are in cm⁻¹.

$\bar{\sigma}_{\text{PB}}$ with $\sigma_{\text{PB}}(\bar{E}_{\text{kin}})$. As it can be seen the differences are appreciable only at the lowest temperature and decrease significantly as the temperature increases because (see Fig. 3) σ_{PB} becomes a slowly varying function of the kinetic energy as the latter increases. At 173 and 297 K the estimated maximum relative error is smaller than 4%.

This observation, already noticed in Refs. 49–51 for other cases and in Refs. 12 and 52 for the C₂H₂-Ar system, allows to perform CC calculations even for heavy systems like those involving Kr and Xe, without performing the time consuming thermal averaging. Specifically, the $R(23)$ and $R(26)$ lines of acetylene broadened by Kr and all the lines broadened by Xe at the kinetic energies=153 and 263 cm⁻¹

FIG. 4. Normalized collisional HWHM γ_0 for the Kr-C₂H₂ system. Comparison among thermally averaged (circles) and unaveraged (continuous lines) values.

FIG. 5. Experimental and calculated PB coefficients for the Xe–C₂H₂ system. Solid lines: present CC/CS calculations; white circles: *P* lines at 297 K from Ref. 26; black circles: *R* lines at 297 K from Ref. 25; black squares: *P* lines at 297 K from Ref. 15; gray squares: *R* lines at 297 K from Ref. 15; white triangles: results at 173 K from Ref. 26. $m = -j$ in a *P* branch and $m = j + 1$ in an *R* branch.

were calculated within such an approximation. Even if it is not obvious to assess the accuracy of our results for the C₂H₂–Xe system we expect calculated σ_{PB} to be accurate to within a few percents.

TABLE III. Calculated and measured pressure broadening coefficients for the Kr–C₂H₂ system at $T=297$ K. $m=j+1$ (*R* lines) and $m=j$ (*P* lines). Results are in $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$.

<i>M</i>	Calc.	<i>P</i> Voigt	<i>R</i> Rautian	<i>R</i> Voigt	<i>R</i> Rautian
1	95.15	82.8(2.0)	85.9(2.7)		
2	87.25	76.7(1.8)	80.8(2.0)	77.4(2.9)	80.9(2.9)
3	81.20				
4	75.80				
5	69.00			62.3(1.6)	65.7(2.3)
5				61.8(1.7)	64.3(1.5)
6	66.00			61.3(1.7)	64.6(2.0)
7	61.45			57.7(1.6)	62.2(2.6)
8	59.20			57.4(1.3)	60.1(2.0)
9	58.10				
10	57.35			52.6(1.5)	59.9(1.7)
11	56.65			52.4(2.0)	54.8(1.9)
12	55.70			50.2(1.6)	53.6(1.7)
13	54.55				
14	53.40				
15	51.70			46.0(1.6)	49.0(1.9)
16	50.20				
17	48.80			43.0(1.4)	47.4(1.7)
18	47.20				
19	45.60				
20	44.05				
21	41.50				
22				36.8(1.3)	40.6(1.3)
23					
24	36.80			34.8(0.8)	39.0(2.0)
27	32.60			29.2(1.4)	34.8(1.1)

TABLE IV. Calculated and measured pressure broadening coefficients for the Kr–C₂H₂ system at $T=173$ K. Results are in $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$.

<i>M</i>	Calc.	<i>P</i> Voigt	<i>P</i> Rautian	<i>R</i> Voigt	<i>R</i> Rautian
1	137.85	123.3(3.4)	125.3(4.0)		
2	127.15	114.0(3.4)	119.2(4.5)	115.2(2.9)	118.3(3.5)
3	119.22				
4	110.80				
5	103.08			97.2(2.7)	100.5(2.6)
6	98.02			91.9(3.3)	94.3(3.2)
7	93.27			88.3(2.4)	91.9(3.2)
8	90.81			85.4(2.2)	86.9(2.3)
9	89.42				
10	88.17			84.1(2.4)	86.1(3.4)
11	86.48				
12	84.35			79.2(1.6)	80.4(1.6)
13	81.96				
14	79.47				
15	76.52			72.3(2.4)	74.6(2.1)
16	73.79				
17	71.37			67.4(2.4)	71.0(2.3)
18	68.65				
19	65.87				
20	63.34				
21	58.16				
22				53.6(2.3)	57.2(1.4)
24	50.25			48.7(2.4)	52.8(1.6)
27	43.44				

Results of these calculations are reported in Figs. 2 and 5 and in Tables III–V (and will be discussed in Sec. VII).

VI. BOUND STATES AND SPECTRAL FEATURE CALCULATIONS

We have used the BOUND package⁵³ for calculating bound-state vibration-rotation energy levels for C₂H₂–Ar,

TABLE V. Calculated pressure broadening coefficients for the Xe–C₂H₂ system, at $T=296$ K and $T=173$ K. Results are in $10^{-3} \text{ cm}^{-1} \text{ atm}^{-1}$.

<i>M</i>	$T=297$ K	$T=173$ K
1	109.20	154.05
2	98.70	136.55
3	91.00	132.20
4	83.45	121.55
5	76.75	113.90
6	71.80	106.90
7	67.40	102.55
8	63.40	101.40
9	62.20	100.60
10	61.85	98.75
11	60.85	95.80
12	59.25	92.40
13	57.55	88.55
14	55.80	83.25
15	53.95	80.60
16	52.00	75.95
17	50.05	72.55
18	48.00	69.75
19	45.85	66.25
20	43.95	63.00
21	43.35	61.30

C₂H₂-Kr, and C₂H₂-Xe systems, exploiting the atom-bond PESs obtained in the present work. The coupled equations, which arise when any of the potential energy surfaces determined in the previous section are inserted into the Schrödinger equation, can be tackled exactly (apart from the neglect of intramonomer vibration). A complete description of the coupled-channel bound-state method has been given by Hutson.⁵⁴ The angular functions were expanded in a space-fixed basis set, including all monomer functions up to $j_{\max}=40$, and treating C₂H₂ as a rigid rotor, with the same rotational constant value as given in Sec. V. The reduced masses of the complexes were taken to be 15.7575, 19.8587, and 21.7132 u, respectively. The resulting close-coupled equations were solved by numerical propagation from $R_{\min}=2.45$ Å to $R_{\max}=16.45$ Å using the diabatic modified log-derivative method of Manolopoulos⁵⁵ with an interval size of 0.0035 Å. The resulting energy levels are converged to better than 10^{-6} cm⁻¹.

A rotational-vibrational scheme based on the permutation-inversion symmetries has been used here rather than the usual point group. Since in our work we treat acetylene as a rigid rotor not all permutations are feasible. The rotation-vibration wave functions of the C₂H₂-rare gas complexes may be classified according to the value of total angular momentum J , rotational angular momentum j , and the total parity $p=(-1)^{j+l}$ quantum numbers. The symmetries of the close coupling basis functions (under the molecular symmetry group C_{2v}) are consistent with those described in Ref. 17.

An interesting aspect of the calculations is the possibility to recover some spectral features of the systems from some transitions allowed between the calculated bound states. Since the BOUND program performs a full dimensional calculation, the energy levels obtained include centrifugal distortion effects and any dynamical contributions. In comparing them with experiment, it is convenient to define energy differences that may be qualitatively interpreted in terms of rigid-molecule rotational constants and prolate near-symmetric top centrifugal distortion constants, as proposed by Hutson and Thornley.¹⁷ The effective rotational constants, zero point energies, and bending frequencies calculated for the three van der Waals complexes are reported in Table VI.

VII. DISCUSSION

The calculated scattering cross sections for the Kr-C₂H₂ system are reported in Fig. 1 (full line) and compared with the experimental results. In Fig. 1 we also report cross sections calculated within the spherical and molecular regimes discussed above. The general behavior of the experimental data, including the absolute value of the cross section, is well reproduced by the calculations. As in the case of the Kr-C₂H₄ complex previously studied⁵⁶ the amplitude of the quantum oscillations in the experimental cross sections looks quenched with respect to the calculated ones. This effect is due to both the high reduced mass of the system and the strong interaction, which make the frequency of the glory undulations high and thus difficult to be observed experi-

TABLE VI. Comparison of experimental and calculated rotational constants (A , B , and C) and bending frequencies ν for the van der Waals ground states of Rg-C₂H₂. Ground state energies (E_0) and zero point energies (ZPEs) are also reported. All the entries are in cm⁻¹.

	Present	Expt.	A-500 ^a	HFD-4 ^b	Barker-M ^c
C ₂ H ₂ -Ar					
E_0	-113.8		-116.7	-144.9	
ZPE	23.3				
A	1.315 9	1.5864 ^d , 1.4011 ^e	1.615 8	1.475 9	1.514
B	0.068 96	0.06922 ^{d,e}	0.069 85	0.068 94	0.069 26
C	0.063 94	0.061 95 ^{d,e}	0.061 44	0.062 29	0.062 02
ν	12.63	8.9 ^e , 6.22 ^b	5.301	6.238 4	6.449 4
C ₂ H ₂ -Kr					
E_0	-138.0				
ZPE	22.3				
A	1.309 2				
B	0.051 73				
C	0.048 86				
ν	12.69				
C ₂ H ₂ -Xe					
E_0	-165.5				
ZPE	24.3				
A	1.281 5				
B	0.044 32				
C	0.042 31				
ν	15.42				

^aReference 17.

^bReference 9.

^cReference 18.

^dReference 7.

^eReference 6.

mentally. However, the glory maximum at the highest collision velocity, which suffer less of the quenching effect, is clearly resolved and reproduced by the calculated cross sections.

Furthermore, the obtained PES has been employed to calculate pressure broadening coefficients for this system, as done previously for mixtures in Ar (Ref. 12) and in He.⁵⁷ The results are plotted in Fig. 2 and detailed in Tables III and IV for the two temperatures investigated. As can be seen the overall agreement between calculations and measurements is very satisfactory. In Fig. 2, our experimental and calculated data, at room temperature, are also compared with the experimental values of Bouanich *et al.*²⁴ and Valipour and Zimmermann.¹⁵ The present data are in general agreement with the older measurements performed in Bouanich *et al.*²⁴ while the values measured by Valipour and Zimmermann¹⁵ are clearly higher, in particular, for j larger than about 7, and show an important scatter of the data (especially when one considers the values of R and P lines as reported in Table V of Ref. 15). This discrepancy is similar to those already noticed and discussed in Ref. 12 for the Ar-broadened lines of acetylene and in Ref. 13 for mixtures in helium.

Finally, in Fig. 4 calculations performed at $T=77$ and 400 K are reported. Thermally averaged values between these two temperatures are available on request. This may be useful to retrieve the temperature dependence of the HWHM for $j=0-20$ (see, for instance, Eq. (3) of Ref. 52) in this temperature range.

The interaction of the acetylene molecule with xenon is more attractive at long range than with krypton because of the larger polarizability of xenon.²⁸ This leads for the Xe case to larger pressure broadening cross sections and because the relative speeds are quite similar the Xe-broadened coefficients are the largest [see Eq. (5.3)]. As can be seen in Fig. 5 the pressure broadening coefficients calculated using the present Xe-C₂H₂ PES are in quite good agreement, for low or moderate j values, with the experimental values measured at both room temperature as well as at 173 K in Lance *et al.*^{25,26} The calculated values are detailed in Table V. The agreement with the values reported by Valipour and Zimmermann¹⁵ is still much poorer (see above). The discrepancy observed between the calculated results and the experimental values of Lance *et al.*²⁶ as j increases indicate that the anisotropy of the repulsive part of the present PES at higher energies is not well determined. This is not surprising since the empirical correlation formulas employed to obtain the parameters of the PES are valid at intermediate and long intermolecular distance ranges, and consequently can provide an accurate estimate only of the first onset of the repulsive wall.

Very recently rare gas broadening of acetylene lines has been measured at room temperature at the university of Oregon.⁵⁸ These new data confirm our analysis.

The potential parameters of the various atom-bond additive pairs, defining the PESs of all the systems studied in this work, are reported in Table I. The potential curves corresponding to the limiting parallel ($\theta=0$) and perpendicular ($\theta=\pi/2$) geometries and the effective low helicity V_{LH} and high helicity V_{HH} interactions are plotted in the upper panels

FIG. 6. Upper panel: Cuts of the PES of the Kr-C₂H₂ complex, for the limiting $V_{\perp}$ ($\theta=\pi/2$) and $V_{\parallel}$ ($\theta=0$) geometries. The effective low helicity V_{LH} and high helicity V_{HH} potential curves are also shown [see Eqs. (4.2) and (4.3)]. Lower panel: Angular dependence of the PES at two fixed R values.

of Figs. 6 and 7 for Kr-C₂H₂ and Xe-C₂H₂, respectively. In the lower panels of the same figures, angular dependencies of the PESs are shown for two fixed intermolecular distances R , describing typical behaviors in the well region and in the long distance range, respectively. The spherical potentials $\bar{V}(R)$ for all the systems are compared in Fig. 8. Table II lists the main features of the PESs (well depths D_e and equilibrium distance R_e). An absolute minimum of the interaction energy for all the three complexes has been found at the T-shaped ($\theta=\pi/2$) geometry. This is at variance with what is found for the lighter He and Ne complexes which show the absolute minimum for a bent geometry. This can be attributed to the very weak interaction anisotropy of the lighter complexes compared to the much larger anisotropies shown by the heavier systems, especially those involving Kr and Xe. However, the angular dependence of the interaction energy is rather flat around $\theta=\pi/2$ also for Kr-C₂H₂ and Xe-C₂H₂, especially for intermolecular distances in the region of the well depth (see the lower panels of Figs. 6 and 7). Therefore, even if calculated zero point energies (ZPEs) are not so large (see Table VI), one can expect the rare gas atoms to be able to exploit large amplitude motion around the T-shape geometry. This is consistent with the experimental finding of an equilibrium geometry located at $\theta=66^\circ$ for the Ar complex.

FIG. 7. As in Fig. 6, for the Xe-C₂H₂ complex.

As anticipated, some spectral features of the interaction complexes, namely, ground rotational state energies, ZPEs, and rotational constants, have been calculated in the present work, and are summarized in Table VI. The only comparison possible with previous data is for the Ar-C₂H₂ system. To this aim we faced the problem of a large number of very different PESs, available in the literature (see, for example, Refs. 17 and 19), which make a global comparison time (and space) consuming and also scarcely significant. To this regards it is also worth to note that several mistakes are present

FIG. 8. Spherical average potential curves $\bar{V}$ [see Eq. (4.1)], for the studied systems.

in more than one paper, quoting the original values of the rotational constants of Ar-C₂H₂ complex as measured by Hu *et al.*,⁷ certainly not helping the comparison of the literature data. Herein, we decided to compare our results with experimental ones and with values obtained from other empirical or semiempirical PES, considering that an exhaustive discussion of the theoretical works has been presented in Ref. 21. We stress that at variance with the other studies our PES has not been fitted to the spectroscopic data. In view of this fact we consider fully acceptable the agreement of Table VI. Specifically, the present value of the bending frequency, larger than the experimental ones, seems to indicate an anisotropy of interaction too high, at least in the well region. More generally, for the three acetylene-rare gas complexes, we found *A* rotational constants much larger than the *B* rotational constant of the free acetylene molecule (1.177). This confirms that all the three complexes are not rigid T-shaped, even if in going from Ar to Xe the trend is for an increased rigidity, which is also suggested by an increased angular anisotropy. The ZPEs show similar values for the three systems but their relative values (with respect to the binding energies) decrease from 17% for the Ar complex to 14% and 12% for the Kr and the Xe complexes, respectively. This is also in line with a more rigid structure for the heavier complexes.

VIII. CONCLUSIONS

The acetylene-rare gas complexes are prototype of van der Waals systems involving an apolar molecule with a triple bond. Nevertheless, the potential energy surfaces of only the lighter He, Ne, and Ar systems have been characterized in the past. In this work we completed the study characterizing the complexes of acetylene with the heavier krypton and xenon atoms. Specifically, integral cross sections and pressure broadening coefficients have been measured for the Kr-C₂H₂ weakly bound system. A PES of the atom-bond additive pairs has been generated and some of its parameters have been optimized to reproduce the experimental values. To this aim accurate calculations of both the scattering and pressure broadening cross sections have been carried out. A similar PES has then been obtained for Xe-C₂H₂ by an empirical scaling of the parameters of the Kr-C₂H₂ system. Pressure broadening coefficients have been calculated obtaining a good agreement with experimental data. Finally, these PES together with a similar one, previously determined by the same authors for the Ar-C₂H₂ case, have been employed to characterize some spectral features of these weakly bound van der Waals complexes. The calculations suggest that all the complexes may undergo large amplitude motions around the equilibrium geometry but that the rigidity increases in going from Ar to the heavier Kr and Xe cases.

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