

Simple semi-classical model of pressure-broadened infrared/microwave linewidths in the temperature range 200–3000 K

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ABSTRACT

There is a need for line broadening parameters for molecules found in exoplanetary atmospheres for a variety of broadeners and a range of temperatures. The use of an easily handled semi-classical theoretical expression is suggested for the calculation of pressure-broadened linewidths for (vib)rotational transitions over a large temperature range (200–3000 K) starting from a minimal set of input parameters: kinetic molecular properties and the character of the leading term in the intermolecular interaction potential. Applications to NO and OH colliding with rare-gas atoms and non-polar molecules demonstrate good consistency with available measurements over the full indicated temperature range. The procedure therefore can be expected to provide realistic estimates for line broadening of “exotic” molecules and molecular ions present in hot planetary atmospheres.

Key words: algorithms – data methods – exoplanets – line profiles

1 INTRODUCTION

The characterisation and modelling of exoplanetary atmospheres requires large volumes of laboratory spectroscopic data (Tennyson & Yurchenko 2018; Hedges & Madhusudhan 2016; Gandhi et al. 2020; Grimm et al. 2021). While there are a number of projects dedicated to the production of extensive line lists of molecular line positions and transition probabilities (Tennyson et al. 2020; Rey et al. 2016; Bernath 2020; Huang et al. 2021), the provision of the associated parameters to quantify the effects of line broadening is much less well developed. Simulations have demonstrated the need to deal correctly with line broadening in the atmospheres of exoplanets (Tinetti et al. 2012; Amundsen et al. 2014; Anisman et al. 2022). The provision of these line broadening parameters was identified as the most important requirement by Fortney et al. (2019) in their review of needs for laboratory measurements and ab initio studies to aid understanding of exoplanetary atmospheres. While some crude attempts have been made to provide general procedures to produce the volume line broadening data required, such as that by Barton et al. (2017), there is an outstanding need for these data for a wide range of molecules, temperatures and broadeners.

Current spectroscopic data needs for studies of hot atmospheres include at least qualitative estimates of pressure-broadening parameters for many “exotic” molecules and molecular ions, including those forming solely at very elevated temperatures. The variety of exoplanet atmospheres being probed suggest that while in gas giants the main perturbing partners are hydrogen (H₂) and helium (He), a whole range of other broadeners including carbon dioxide (CO₂), nitrogen (N₂), oxygen (O₂), water vapor (H₂O), carbon monoxide (CO), nitric oxide (NO), methane (CH₄) and ammonia (NH₃) are of interest too. Due to the occurrence of hot atmospheres and chemical reactions which lead to the formation of spectroscopically active species, laboratory studies of line-shape parameters are very scarce or totally missing for transitions at both infrared/microwave (IR/MW) and visible/ultraviolet (UV) wavelengths which are probed by on-board instruments of space missions or ground-based telescopes.

In this paper we suggest and test the use of a simple theoretical expression as the means of providing reasonable estimates of pressure-broadened line widths of vibration-rotation and pure rotation transitions which largely lie in the IR/MW frequency domain.

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2 WORKING FORMULA

The line shapes of exoplanet vibration-rotation spectra are generally modelled using Voigt profiles, which assume statistical independence of two main broadening mechanisms: Doppler broadening due to the thermal motion of the spectroscopically active species and pressure broadening induced by collisions with surrounding particles. Consequently, the Voigt profile is a convolution of a Gaussian profile characterized by the Doppler width (straightforward to compute) and of a Lorentzian profile having the pressure-broadening width which depends on the active molecule (a), the perturber (p) and the temperature (T). In principle, this pressure-broadening width also varies between individual transitions. Here we simply consider means of estimating its value and temperature dependence for different collision pairs.

Unlike electronic absorption bands, line shapes of vibration-rotation and pure rotation transitions are mostly influenced by inelastic collisions, i.e., those inducing non-radiative transitions among the internal states of the active molecule. This key feature was first noted by [Anderson \(1949\)](#) who included “on-resonance” exchange of energy quanta between pairs of levels in the identical active and perturbing molecules. Later, Anderson’s theory was systematized and extended to non-resonant interactions by [Tsao & Curnutte \(1962\)](#). In their analysis of the close-collisions contribution to the second-order scattering matrix S_2 responsible for line broadening, these authors derived an approximate expression for γ , the collisional half-width-at-half-maximum (HWHM) of intensity, as a sum of two terms.

The first term comes from “strong” collisions corresponding to small values of the impact parameter b . As such collisions interrupt the radiation completely as the active molecule leaves its initial state, here S_2 is set to 1 and the critical (“cut-off”) value b_0 for the impact parameter is defined by the condition $S_2(b_0) = 1$. Assuming the same b_0 for all rotational states of the perturber, calculation of the cross section $\sigma = \int S_2(b) 2\pi b db$ for b ranging from 0 to b_0 gives $\gamma = nv\sigma/(2\pi c)$ in cm^{-1} which leads to

$$\gamma_{0 \rightarrow b_0} = \frac{nv}{2c} b_0^2, \quad (1)$$

where n is the number density of perturbing particles, v is the mean relative speed, and c is the speed of light. The second term, the contribution from “weak” (distant) collisions corresponding to $b > b_0$, can be estimated from the $S_2(b)$ dependence of the leading interaction in the anisotropic intermolecular potential, which typically varies as b^{-m} ($m = 4, 6, 8, 10$ for dipole-dipole, dipole-quadrupole, quadrupole-quadrupole and dipole-“induced dipole” interactions, respectively), so that

$$\gamma_{b_0 \rightarrow \infty} = \frac{nv}{(m-2)c} b_0^2. \quad (2)$$

We emphasize that the m -value should not be confused with the power q of the inverse intermolecular-distance dependence in the interaction-potential R^{-q} : for the straight-line trajectories used by Anderson they are related by $m = 2(q - 1)$. Taking account of the full b -range results in

$$\gamma = \frac{m}{(m-2)} \frac{nv}{2c} b_0^2. \quad (3)$$

This expression can be made more explicit by using n corresponding to 1 atm and the dependence of v on the absolute temperature T (in K) and on the masses of the active (m_a) and perturbing (m_p) molecules (in Dalton):

$$n = \frac{N_A}{V_{\text{1mole}}} = 7.3385 \cdot 10^{21} \frac{1}{T} \text{ cm}^{-3}, \quad (4)$$

$$v = \sqrt{\frac{8kT}{\pi m^*}} = 1.455 \cdot 10^4 \sqrt{T} \sqrt{\frac{m_a + m_p}{m_a m_p}} \text{ cm s}^{-1}, \quad (5)$$

where the standard notations are employed for the Avogadro number N_A , one-mole volume V_{1mole} , Boltzmann’s constant k , and reduced mass m^* . Substituting the above formulae in Eq. (3) and assuming b_0 is given in picometres, we get the half-width in the commonly used units of $\text{cm}^{-1} \text{ atm}^{-1}$:

$$\gamma = 1.7796 \cdot 10^{-5} \frac{m}{(m-2)} \frac{1}{\sqrt{T}} \sqrt{\frac{m_a + m_p}{m_a m_p}} b_0^2. \quad (6)$$

The remaining point concerns the choice of a reasonable estimate for b_0 . [Tsao & Curnutte \(1962\)](#) suggested using the kinetic diameter d as b_0 . Although d is a characteristic averaged over all collisions, in the following we test this choice for various kinds of molecular pairs.

3 APPLICATION TO NEUTRAL MOLECULES

Line lists for open-shell diatomics NO ([Qu et al. 2021](#)) and OH ([Bernath 2020](#)) are included in the ExoMol database ([Tennyson et al. 2020](#)); these species were chosen as active molecules. Their permanent electric dipole moments differ by an order of magnitude: $\mu_{\text{NO}} = 0.158 \text{ D}$ ([Stogryn & Stogryn 1966](#)) and $\mu_{\text{OH}} = 1.668 \text{ D}$ ([Meerts & Dymanus 1973](#)). This allows us to test both cases of weakly polar and strongly polar active molecules. Moreover, experimental linewidths are available for these species perturbed by different partners over wide temperature ranges which allows comparisons with our predictions. Here we

Table 1. Tabulated kinetic diameters (or Lennard-Jones parameters) used in calculations, taken from ‘12Ba’ (Baker 2012), ‘82KhBo’ (Khayar & Bonamy 1982) and ‘14JaMi’ (Jasper & Miller 2014).

	NO	OH	N ₂	O ₂	H ₂	He	Ar
d (pm)	317 [12Ba]	336 ^a [82KhBo]	368 [14JaMi]	346 [14JaMi]	292 [14JaMi]	258 [14JaMi]	333 [14JaMi]
m_a/p (amu)	30	17	28	32	2	4	40

^a Deduced from OH-N₂ (Khayar & Bonamy 1982) and N₂ (Jasper & Miller 2014) data by combination rules.

consider N₂, O₂, H₂ (with the quadrupole moments $Q_{N_2} = -1.52$ DÅ, $Q_{O_2} = -0.39$ DÅ, $Q_{H_2} = 0.66$ DÅ (Stogryn & Stogryn 1966)) but also He and Ar (polarizabilities $\alpha_{He} = 0.208$ Å³, $\alpha_{Ar} = 1.662$ Å³ (Olney et al. 1997)) as representative perturbers for astrophysical applications. Additionally, this choice of species also provides a check on the influence of the perturber/radiator mass ratio. We need to consider two types of leading interactions: dipole-quadrupole ($m = 6$) for perturbation by N₂, O₂, H₂ and dipole-‘induced dipole’ ($m = 10$) for perturbation by He and Ar. The corresponding half-widths follow from Eq. (6):

$$\gamma = 2.6694 \cdot 10^{-5} \frac{1}{\sqrt{T}} \sqrt{\frac{m_a + m_p}{m_a m_p}} d^2 \quad \text{for } m = 6, \quad (7)$$

$$\gamma = 2.2245 \cdot 10^{-5} \frac{1}{\sqrt{T}} \sqrt{\frac{m_a + m_p}{m_a m_p}} d^2 \quad \text{for } m = 10. \quad (8)$$

For our case of different active and perturbing molecules the kinetic diameter should be taken as a sum of kinetic radii of collision partners: $d = (d_a + d_p)/2$. The values of d_a and d_p used in our calculations are gathered in Table 1. In the cases where kinetic diameters were unavailable, Lennard-Jones parameters σ_{LJ} were used instead.

Theoretical estimates obtained with Eqs. (7,8) and the data of Table 1 are compared to experimental values in Table 2. It is worth mentioning that experimental data for (vib)rotational transitions in the IR/MW regions generally demonstrate quite pronounced dependence on the rotational quantum number (except when the perturber is very light, such as He and H₂), so we selected ‘mean’ experimental results (corresponding to intermediate values of the rotational quantum number or averaged on the rotational numbers). For almost all the molecular pairs considered and all temperatures, very satisfactory agreement is found. The one exception is the NO-He case, where the theoretical estimate is double the measured value. This discrepancy can be ascribed to the small values of the NO dipole moment and He polarizability as well as to the small He mass: the dipole-‘induced dipole’ term is unable to mimic the NO-He interaction within the classical-path approximation. However, with increasing temperature the use of classical trajectories becomes better justified, so even for perturbation by He Eqs. (7) and (8) as well as the general expression of Eq. (6) are expected to yield predictions of accuracy better than 50%. We note that for the strongly polar OH radical the use of Eq. (8) even for the light collision partner He leads to reliable approximation of the intermolecular interaction by the leading term judged by comparison with the experimental data (Bastard et al. 1979) at 296 K. The measurements provided for OH by Park et al. (1999) are significantly lower than the results of other authors, so we consider the factor of four difference found between their measurements for OH-He and our theoretical value at 194 K to be questionable. Finally, the power -0.5 for the T -dependence given by Eq. (6) is confirmed for NO-N₂ and NO-Ar by the measurements of Almodovar et al. (2017) over the temperature interval 1000–3000 K.

For completeness, we note that in the absence of measured and/or calculated line-broadening data some authors use a formula arising from the kinetic gas theory (Dodge et al. 1980; Murzyn et al. 2022). Indeed, the mean frequency of molecular collisions, i.e. the average number of collisions per second or the inverse of the free path time τ , can be written as

$$\tau^{-1} = \pi \varnothing^2 n v, \quad (9)$$

where \varnothing denotes the collision diameter (called also optical diameter) and the other variables have the same meaning as in Eq. (1). Eq. (9) assumes that the foreign-gas pressure is much higher than the pressure of the active gas, so that no collisions occur between pairs of active molecules. τ^{-1} gives the collisional line half-width in angular frequency units. Converting this half-width to cm⁻¹ at 1 atm pressure, we get

$$\gamma_{km} = \frac{\tau^{-1}}{2\pi c} = \frac{n}{2c} \sqrt{\frac{8kT}{\pi m^*}} \varnothing^2 = 1.7796 \cdot 10^{-5} \frac{1}{\sqrt{T}} \sqrt{\frac{m_a + m_p}{m_a m_p}} \varnothing^2. \quad (10)$$

As mentioned by Weisskopf (1933), the collision diameter \varnothing is much larger than the kinetic diameter d . For example, the use of Eq. (10) in fits of Lorentzian lines in the $\gamma(0,0)$ band of NO perturbed by N₂, CO₂, CO, CH₄ and Ar (Dodge et al. 1980) resulted in the optical collisions diameters about 3 times bigger than literature values obtained from viscosity measurements. However, the current point of view (Kunze et al. 2022) is rather that different kinds of ‘molecular diameters’ manifest themselves in different physical processes and are probed by different experimental techniques, so that the term ‘collision diameter’ is also used as an equivalent of ‘kinetic diameter’ (Albrecht et al. 2003). Assuming the equivalence of d and \varnothing , Eqs (6) and (10) differ solely by the ratio $m/(m-2)$ which ‘corrects’ the kinetic (‘hard-sphere’) approach by accounting for the leading intermolecular interaction term. The line half-widths obtained by Eq. (10) are added to the calculated values of Table 2 between parentheses. They demonstrate less good agreement with the measurements, therefore the use of Eq. (6) is clearly preferable.

Table 2. Comparison of estimated collisional half-widths γ (in $\text{cm}^{-1} \text{atm}^{-1}$) with measurements. Experimental data are taken as averaged or characteristic values for mid-range rotational quantum numbers. Calculated values between parentheses correspond to the kinetic “hard-sphere” model. The experimental data are from ‘83HoBo’ (Houdeau et al. 1983), ‘19AlSu’ (Almodovar et al. 2019), ‘99AlDaMa’ (Allout et al. 1999), ‘91LiLiLi’ (Liu et al. 1991), ‘99PaZiCh’ (Park et al. 1999), ‘96PaZi’ (Park et al. 1996), ‘91ChJe’ (Chance et al. 1991), ‘79BaBr’ (Bastard et al. 1979), ‘79BuCl’ (Burrows et al. 1979) and ‘17Da’ (Dagdigian 2017).

		N ₂		O ₂		H ₂		He		Ar	
		calc.	expt	calc.	expt	calc.	expt	calc.	expt	calc.	expt
NO	163 K	0.065	0.080	0.058	0.095 ^a						
		(0.043)	[83HoBo]	(0.039)							
	296 K	0.048	0.055	0.043	0.050			0.057	0.024 ^c	0.033	0.040
		(0.032)	[19AlSu]	(0.029)	[99AlDa]			(0.046)	[91LiLi]	(0.026)	[19AlSu]
802 K	0.029	0.024							0.020	0.017	
	(0.019)	[19AlSu]							(0.016)	[19AlSu]	
1000 K	0.026	0.025							0.018	0.015	
	(0.017)	[19AlSu]							(0.014)	[19AlSu]	
OH	194 K	0.073	0.112 ^b	0.055	0.067	0.141	0.108	0.078	0.019	0.052	0.070
		(0.049)	[99PaZi]	(0.037)	[99PaZi]	(0.094)	[99PaZi]	(0.062)	[99PaZi]	(0.042)	[96PaZi]
	296 K	0.059	0.068	0.045	0.050	0.114	0.104	0.063	0.076	0.042	0.050
		(0.039)	99PaZi	(0.030)	[91ChJe]	(0.076)	[79BaBr]	(0.050)	[79BaBr]	(0.034)	[79BuCl]
500 K				0.035	0.089			0.015			
				[99PaZi]	[99PaZi]			[99PaZi]			
									0.032	0.045 ^d	
									(0.026)	[17Da]	

^a Theoretical result (Buldyreva et al. 2001) giving a good agreement with room-temperature measurements (Allout et al. 1999).

^b Data for very low rotational quantum number.

^c Obtained for ¹⁵NO.

^d Quantum scattering calculations for MW transitions averaged over rotational quantum numbers.

It should be also noted that for kinetic/collision diameters not measured experimentally, Loukhovitski & Sharipov (2021) suggested a semi-empirical formula for their calculation from electronic polarizabilities: $d = p_1 + p_2\alpha^{1/3}$, where $p_1 = 0.768 \text{ \AA}$ and $p_2 = 2.168$ (d here is obtained in \AA and should be multiplied by 100 to be expressed in pm). This formula gives a d -estimate coinciding with the value of Table 1 for Ar, slightly different results for N₂, O₂, H₂, and a nearly 20 % lower value for He. However, for small-size collision partners considered here, the diameters are generally available from measurements, so that the semi-empirical formula given above can be more useful for considering large polyatomic collision partners.

4 IONIC MOLECULES

It is also important to consider molecular ions whose spectra and hence line broadening are thought to become important at the top of exoplanetary atmospheres (Bourgalais et al. 2020). Observation of rotational spectra of molecular ions (Woods (1983) and references therein) demonstrates that their pressure-broadened linewidths are similar or slightly larger than those of corresponding neutral molecules.

Most semi-classical theories published in the literature deal with neutral species. However, Buffa et al. (1994) extended the semi-classical Anderson-Tsao-Curnutte (ATC) theory to the case of molecular ions colliding with neutral perturbers. They argued that the interaction between the ion charge and the multipole moments (permanent or induced) of the perturber does not contribute to collisional broadening but affects the trajectory (if curved trajectories are used instead of the straight-line paths) and induces a polarization on the neutral collision partner. This is the dipole moment induced on the perturber by the ionic monopole which interacts with the dipole moment of the ionic monopole and gives the dominant contribution to the collisional broadening in the case of HCO⁺ colliding with Ar, for example. The dipole-“monopole-induced dipole” interaction varies as R^{-5} , and we get

$$\gamma = 2.3728 \cdot 10^{-5} \frac{1}{\sqrt{T}} \sqrt{\frac{m_a + m_p}{m_a m_p}} d^2 \quad \text{for } m = 8. \quad (11)$$

If the collision partner is a non-polar diatomic (e.g., H₂), Eq. (7) for dipole-quadrupole interactions applies.

We have attempted some linewidth estimates (Table 3) for ionic active molecules interacting with homonuclear diatomics (H₂) and rare gases (He, Ar). Molecular ions NO⁺ and HCO⁺ with permanent dipole moments absorbing in the IR/MW regions were chosen. However, for these molecular systems measurements and advanced calculations published in the literature correspond to low temperatures (typically far below room temperature), where semi-classical approaches lose their validity. In particular, orbiting collisions (capture effects) not accounted for by the ATC approach occur, so that our estimates are already expected to be lower than measurements. A possible criterion to check the applicability of semi-classical treatment for

Table 3. Comparison of estimated collisional half-widths γ (in $\text{cm}^{-1} \text{atm}^{-1}$) with measurements or independent calculations for ionic active molecules in collision with H_2 , He and Ar.

	calc. with Eqs. (7) or (11)	expt/other
NO^+-H_2 300K	0.078 ($d = 264$ pm) 0.083 ($d = 271$ pm)	0.05 ^a (López-Puertas et al. 2006)
HCO^+-H_2 100 K	0.180 ($d = 304$ pm)	0.750 ^b (Anderson et al. 1980)
HCO^+-H_2 300 K	0.104 ($d = 304$ pm)	0.310 (Liao & Herbst 1996)
HCO^+-He 88 K	0.111 ($d = 287$ pm)	0.313 ^c (Buffa et al. 2008)
HCO^+-Ar 77 K	0.069 ($d = 324.5$ pm)	0.369 ^c (Buffa et al. 1994)

^a Rough estimate from Fig. 2 of López-Puertas et al. (2006).

^b $J = 1 - 0$ line

^c $J = 4 - 3$ line

a given temperature is the isotropic potential depth ε (in K). For temperatures higher than ε the relative kinetic energy is big enough, and capture effects are negligible. If the temperature becomes close to or even smaller than ε , an increasing number of molecular complexes is formed and the ATC linewidth is (strongly) underestimated. When available in the literature, we indicated the ε values for the considered molecular pairs, to evaluate the degree of applicability of semi-classical treatments.

For the NO^+-H_2 pair the diameter was taken as $d = 264$ pm (estimated from Fig. 6 of Cabrera-González et al. (2020) as the intermolecular distance corresponding to zero isotropic potential). A more recent study by Orek et al. (2021) of the NO^+-H_2 potential energy surface gives a slightly different value $d = 271$ pm (estimated from their Fig. 5). With respect to a visual estimation $0.05 \text{ cm}^{-1} \text{atm}^{-1}$ from atmospheric spectra (López-Puertas et al. 2006), our estimates with both diameters have the same order of magnitude. We note that the isotropic potential depth for the NO^+-H_2 complex is about 400 cm^{-1} (Cabrera-González et al. 2020), i.e. about 575 K, meaning that the condition for applicability of semi-classical approaches is not respected at 300 K.

In the HCO^+-H_2 case, $d = 316$ pm was deduced for HCO^+ from the intermolecular distance of 287 pm corresponding to the zero isotropic potential of the HCO^+-He system (Buffa et al. 2009) and $d = 258$ pm for He (Table 1); the diameter for the HCO^+-H_2 pair was found therefore to be $d = 304$ pm. For this system the linewidth $\gamma = 29.6 \text{ MHz Torr}^{-1} = 0.750 \text{ cm}^{-1} \text{atm}^{-1}$ of the $J = 1-0$ transition was measured at 100 K (Anderson et al. 1980), which is 4 times bigger than $\gamma = 0.180 \text{ cm}^{-1} \text{atm}^{-1}$ calculated by Eq. (7). The measured value was also considered as unexpectedly three times larger, relatively to a neutral, by Liao & Herbst (1996), but their ATC calculations with more terms in the anisotropic potential resulted finally in a very satisfactory agreement with the experiment (Anderson et al. 1980). The ATC result of Liao & Herbst (1996) for 300 K ($0.310 \text{ cm}^{-1} \text{atm}^{-1}$ deduced from their Fig. 2a) is also 3 times bigger than our estimate $0.104 \text{ cm}^{-1} \text{atm}^{-1}$ with Eq. (7).

Collisional broadening of HCO^+-He rotational lines at 88 K was measured by Buffa et al. (2008). Their linewidth for the $J = 4-3$ transition ($0.313 \text{ cm}^{-1} \text{atm}^{-1}$) is again 3 times higher than the value calculated by Eq. (11) with $d = 287$ pm (Buffa et al. 2009). The isotropic-potential depth (Buffa et al. 2009) is 277.4 cm^{-1} or 399 K, so that the applicability of semi-classical treatment is strongly violated. With Ar as the collision partner, the experimental value for the same transition at 77 K is $14.56(7) \text{ MHz Torr}^{-1} = 0.369 \text{ cm}^{-1} \text{atm}^{-1}$ (Buffa et al. 1994), whereas our calculation with $d = (316 + 333)/2 \text{ pm} = 324.5 \text{ pm}$ yields $0.069 \text{ cm}^{-1} \text{atm}^{-1}$, showing underestimation by a factor of 5. For HCO^+-Ar at 77 K, Buffa et al. (1999) communicated the average capture radius value of 8.7 \AA , which explains this underestimation.

These comparisons with low-temperature measurements demonstrating regular underestimates of line broadening for ionic active molecules confirm the internal coherence of the model: it does not work for temperatures where it is not expected to work. At high temperatures characteristic of hot planetary atmospheres the conditions of applicability of semi-classical approaches are amply satisfied, and linewidth estimates provided by Eq. (11) for He, Ar or by Eq. (7) for H_2 are believed to be quite realistic.

5 CONCLUSION

We propose the use of a simple semi-classical formula for rough estimates of collisional broadening for (vib)rotational molecular transitions occurring at infrared and microwave wavelengths when neither measurements nor calculations are available. Only kinetic molecular diameters and the type of the leading intermolecular interaction are required to get the correct order of magnitude for pressure-broadened linewidths, as demonstrated for neutral active species NO and OH colliding with rare gases and non-polar diatomics in a wide temperature range relevant to hot planetary atmospheres. A theoretical basis is also presented to extend the use of the model to ionic molecules. This approach will be incorporated into an updated ExoMol diet (Barton et al. 2017) to providing default line-broadening parameters when none are available from other sources.

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DATA AVAILABILITY

All data is included in the article

REFERENCES

- Albrecht, E., Baum, G., Bellunato, T., Bressan, A., Dalla Torre, S., D'Ambrosio, C., Davenport, M., Dragicevic, M., Duarte Pinto, S., Fauland, P., Ilie, S., Lenzen, G., Pagano, P., Piedigrossi, D., Tessarotto, F., & Ullaland, O., 2003. VUV absorbing vapours in n-perfluorocarbons, *Nucl. Instrum. Methods Phys.*, **510**(3), 262–272.
- Allout, M.-Y., Dana, V., Mandin, J.-Y., Von der Heyden, P., Décaire, D., & Plateaux, J.-J., 1999. Oxygen-Broadening Coefficients of First Overtone Nitric Oxide Lines, *J. Quant. Spectrosc. Radiat. Transf.*, **61**, 759–765.
- Almodovar, C. A., Spearrin, R. M., & Hanson, R. K., 2017. Two-color laser absorption near 5 μm for temperature and nitric oxide sensing in high-temperature gases, *J. Quant. Spectrosc. Radiat. Transf.*, **203**, 572–581.
- Almodovar, C. A., Su, W.-W., Strand, C. L., & Hanson, R. K., 2019. R-branch line intensities and temperature-dependent line broadening and shift coefficients of the nitric oxide fundamental rovibrational band, *J. Quant. Spectrosc. Radiat. Transf.*, **239**, 106612.
- Amundsen, D. S., Baraffe, I., Tremblin, P., Manners, J., Hayek, W., Mayne, N. J., & Acreman, D. M., 2014. Accuracy tests of radiation schemes used in hot jupiter global circulation models, *A&A*, **564**, A59.
- Anderson, P. W., 1949. Pressure Broadening in the Microwave and Infra-Red Regions, *Phys. Rev.*, **76**, 647–661.
- Anderson, T. G., Gudeman, C. S., Dixon, T. A., & Woods, R. C., 1980. Pressure broadening of the HCO^+ $J = 0 - 1$ transition by hydrogen, *J. Chem. Phys.*, **72**, 1332–1336.
- Anisman, L., Chubb, K. L., Changeat, Q., Edwards, B., Yurchenko, S. N., Tennyson, J., & Tinetti, G., 2022. Cross-sections for heavy atmospheres: H_2O self-broadening, *J. Quant. Spectrosc. Radiat. Transf.*, **283**, 108146.
- Baker, R. W., 2012. *Appendix, Membrane Technology and Applications*, p. 557, John Wiley & Sons, Ltd.
- Barton, E. J., Hill, C., Czurylo, M., Li, H.-Y., Hyslop, A., Yurchenko, S. N., & Tennyson, J., 2017. The ExoMol diet: H-2 and He line-broadening parameters, *J. Quant. Spectrosc. Radiat. Transf.*, **203**, 490–495.
- Bastard, D., Bretenoux, A., Charru, A., & Picherit, F., 1979. Determination of mean collision cross sections of free radical OH with foreign gases, *J. Quant. Spectrosc. Radiat. Transf.*, **21**, 369–372.
- Bernath, P. F., 2020. MoLLIST: Molecular Line Lists, Intensities and Spectra, *J. Quant. Spectrosc. Radiat. Transf.*, **240**, 106687.
- Bourgalais, J., Carrasco, N., Changeat, Q., Venot, O., Javanović, L., Pernot, P., Tennyson, J., Chubb, K. L., Yurchenko, S. N., & Tinetti, G., 2020. Ions in the thermosphere of exoplanets: Observational constraints revealed by innovative laboratory experiments, *ApJ*, **895**, 77.
- Buffa, G., Tarrini, O., Cazzoli, G., & Dore, L., 1994. Broadening and shifts of the lines of molecular ions by collisions with neutral perturbers, *Phys. Rev. A*, **49**, 3557–3565.
- Buffa, G., Tarrini, O., Cazzoli, G., & Dore, L., 1999. Calculations of Argon broadening and shift for HCO^+ rotational lines at 77 K, *J. Chem. Phys.*, **111**, 1870–1874.
- Buffa, G., Dore, L., Tinti, F., & Meuwly, M., 2008. Experimental and Theoretical Study of Helium Broadening and Shift of HCO^+ Rotational Lines, *ChemPhysChem*, **9**, 2237–2244.
- Buffa, G., Dore, L., & Meuwly, M., 2009. State-to-state rotational transition rates of the HCO^+ ion by collisions with helium, *MNRAS*, **397**, 1909–1914.
- Buldyreva, J., Benec'h, S., & Chrysos, M., 2001. Oxygen-broadened and air-broadened linewidths for the no infrared absorption bands by means of the exact-trajectory approach, *Phys. Rev. A*, **63**, 032705.
- Burrows, J., Cliff, D., Davies, P., Harris, G., Thrush, B., & Wilkinson, J., 1979. Pressure broadening of the lowest rotational transition of OH studied by laser magnetic resonance, *Chem. Phys. Lett.*, **65**, 197–200.
- Cabrera-González, L. D., Páez-Hernández, D., & Denis-Alpizar, O., 2020. Relaxation of NO^+ by collision with para- H_2 ($j = 0$), *MNRAS*, **494**, 129–134.
- Chance, K. V., Jennings, D. A., Evenson, K. M., Vanek, M. D., Nolt, I. G., Radostitz, J. V., & Park, K., 1991. Pressure broadening of the 118.455 cm^{-1} rotational lines of OH by H_2 , He, N_2 , and O_2 , *J. Mol. Spectrosc.*, **146**, 375–380.
- Dagdigian, P. J., 2017. Pressure broadening calculations for OH in collisions with argon: Rotational, vibrational, and electronic transitions, *J. Quant. Spectrosc. Radiat. Transf.*, **189**, 105–111.
- Dodge, L., Dusek, J., & Zabielski, M., 1980. Line broadening and oscillator strength measurements for the nitric oxide $\gamma(0,0)$ band, *J. Quant. Spectrosc. Radiat. Transf.*, **24**, 237–249.
- Fortney, J. J., Robinson, T. D., Domagal-Goldman, S., Del Genio, A. D., Gordon, I. E., Gharib-Nezhad, E., Lewis, N., Sousa-Silva, C., Airapetian, V., Drouin, B., Hargreaves, R. J., Huang, X., Karman, T., Ramirez, R. M., Rieker, G. B., Tennyson, J., Wordsworth, R., Yurchenko, S. N., Johnson, A. V., Lee, T. J., Dong, C., Kane, S., Lopez-Morales, M., Fauchez, T., Lee, T., Marley, M. S., Sung, K., Haghghi-pour, N., Robinson, T., Horst, S., Gao, P., you Kao, D., Dressing, C., Lupu, R., Savin, D. W., Fleury, B., Venot, O., Ascenzi, D., Milam, S., Linnartz, H., Gudipati, M., Gronoff, G., Salama, F., Gavilan, L., Bouwman, J., Turbet, M., Benilan, Y., Henderson, B., Batalha, N., Jensen-Clem, R., Lyons, T., Freedman, R., Schwieterman, E., Goyal, J., Mancini, L., Irwin, P., Desert, J.-M., Molaverdikhani, K., Gizis, J., Taylor, J., Lothringer, J., Pierrehumbert, R., Zellem, R., Batalha, N., Rugheimer, S., Lustig-Yaeger, J., Hu, R., Kempton, E., Arney, G., Line, M., Alam, M., Moses, J., Iro, N., Kreidberg, L., Blečić, J., Loudon, T., Molliere, P., Stevenson, K., Swain, M., Bott, K., Madhusudhan, N., Krissansen-Totton, J., Deming, D., Kitiashvili, I., Shkolnik, E., Rustamkulov,

- Z., Rogers, L., & Close, L., 2019. The need for laboratory measurements and ab initio studies to aid understanding of exoplanetary atmospheres, arXiv:1905.07064.
- Gandhi, S., Brogi, M., Yurchenko, S. N., Tennyson, J., Coles, P. A., Webb, R. K., Birkby, J. L., Guilluy, G., & Madhusudhan, N., 2020. Molecular Cross Sections for High Resolution Spectroscopy of super Earths, warm Neptunes and Hot Jupiters, *MNRAS*, **495**, 224–237.
- Grimm, S. L., Malik, M., Kitzmann, D., Guzmán-Mesa, A., Hoeijmakers, H. J., Fisher, C., ao M. Mendonça, J., Yurchenko, S. N., Tennyson, J., Kurucz, R. L., & Heng, K., 2021. HELIOS-K 2.0 and an Open-source Opacity Database for Exoplanetary Atmospheres, *ApJS*, **253**, 30.
- Hedges, C. & Madhusudhan, N., 2016. Effect of pressure broadening on molecular absorption cross sections in exoplanetary atmospheres, *MNRAS*, **458**, 1427–1449.
- Houdeau, J. P., Boulet, C., Bonamy, J., Khayar, A., & Guelachvili, G., 1983. Air broadened NO linewidths in a temperature range of atmospheric interest, *J. Chem. Phys.*, **79**, 1634–1640.
- Huang, X., Schwenke, D. W., & Lee, T. J., 2021. What it takes to compute highly accurate rovibrational line lists for use in astrochemistry, *Acc. Chem. Res.*, **54**, 1311–1321.
- Jasper, A. W. & Miller, J. A., 2014. Lennard-Jones parameters for combustion and chemical kinetics modeling from full-dimensional intermolecular potentials, *Combustion and Flame*, **161**, 101–110.
- Khayar, A. & Bonamy, J., 1982. Calculation of mean collision cross sections of free radical OH with foreign gases, *J. Quant. Spectrosc. Radiat. Transf.*, **28**, 199–212.
- Kunze, S., Groll, J., Besser, B., & Thöming, J., 2022. Molecular diameters of rarefied gases, *Sci. Rep. (Nature)*, **237**.
- Liao, Q. & Herbst, E., 1996. Calculations of the low temperature pressure broadening of HCO⁺ rotational spectral lines by H₂, *J. Chem. Phys.*, **104**, 3956–3961.
- Liu, Z.-A., Liu, Y.-Y., Li, F.-Y., Li, J.-R., He, K.-L., Gong, B.-Z., & Cehn, Y.-Q., 1991. Measurement of pressure broadening coefficients of ¹⁵N¹⁶O by intracavity laser magnetic resonance with a CO laser, *Chem. Phys. Lett.*, **183**, 340–344.
- López-Puertas, M., Flaud, J.-M., Peralta-Calvillo, J., Funke, B., & Gil-López, S., 2006. NO⁺ fundamental and first hot ro-vibrational line frequencies from MIPAS/Envisat atmospheric spectra, *J. Mol. Spectrosc.*, **237**(2), 218–224.
- Loukhovitski, B. I. & Sharipov, A. S., 2021. Molecular Collision Diameters and Electronic Polarizabilities: Inherent Relationship and Fast Evaluation, *J. Phys. Chem. A*, **125**, 5117–5123.
- Meerts, W. L. & Dymanus, A., 1973. Electric dipole moments of OH and OD by molecular beam electric resonance, *Chem. Phys. Lett.*, **23**, 45–47.
- Murzyn, C., Jans, E., & Clemenson, M., 2022. Spears: A database-invariant spectral modeling api, *J. Quant. Spectrosc. Radiat. Transf.*, **277**, 107958.
- Olney, T. N., Cann, N. M., Cooper, G., & Brion, C. E., 1997. Absolute scale determination for photoabsorption spectra and the calculation of molecular properties using dipole sum-rules, *Chem. Phys.*, **223**, 59–98.
- Orek, C., Umiński, M., Kłos, J., Lique, F., Zuchowski, P. S., & Bulut, N., 2021. NO⁺ + H₂: Potential energy surface and bound state calculations, *Chem. Phys. Lett.*, **771**, 138511.
- Park, K., Zink, L., Evenson, K., Chance, K., & Nolt, I., 1996. Pressure broadening of the 83.869 cm⁻¹ rotational lines of OH by N₂, O₂, H₂, and He, *J. Quant. Spectrosc. Radiat. Transf.*, **55**, 285–287.
- Park, K., Zink, L. R., Chance, K. V., Evenson, K. M., & Nolt, I. G., 1999. Pressure Broadening of the 118.455 cm⁻¹ Rotational Lines of OH BY N₂, O₂, H₂, and He, *J. Quant. Spectrosc. Radiat. Transf.*, **61**, 715–716.
- Qu, Q., Yurchenko, S. N., & Tennyson, J., 2021. ExoMol molecular line lists – XLII: Rovibronic molecular line list for the low-lying states of NO, *MNRAS*, **504**, 5768–5777.
- Rey, M., Nikitin, A. V., Babikov, Y. L., & Tyuterev, V. G., 2016. TheoReTS – an information system for theoretical spectra based on variational predictions from molecular potential energy and dipole moment surfaces, *J. Mol. Spectrosc.*, **327**, 138–158.
- Stogryn, D. E. & Stogryn, A. P., 1966. Molecular multipole moments, *Mol. Phys.*, **11**, 371–393.
- Tennyson, J. & Yurchenko, S. N., 2018. The ExoMol atlas of molecular opacities, *Atoms*, **6**, 26.
- Tennyson, J., Yurchenko, S. N., Al-Refaie, A. F., Clark, V. H. J., Chubb, K. L., Conway, E. K., Dewan, A., Gorman, M. N., Hill, C., Lynas-Gray, A. E., Mellor, T., McKemmish, L. K., Owens, A., Polyansky, O. L., Semenov, M., Somogyi, W., Tinetti, G., Upadhyay, A., Waldmann, I., Wang, Y., Wright, S., & Yurchenko, O. P., 2020. The 2020 release of the ExoMol database: molecular line lists for exoplanet and other hot atmospheres, *J. Quant. Spectrosc. Radiat. Transf.*, **255**, 107228.
- Tinetti, G., Tennyson, J., Griffiths, C. A., & Waldmann, I., 2012. Water in Exoplanets, *Phil. Trans. Royal Soc. London A*, **370**, 2749–2764.
- Tsao, C. J. & Curnutte, B., 1962. Line-widths of pressure-broadened spectral lines, *J. Quant. Spectrosc. Radiat. Transf.*, **2**, 41–91.
- Weisskopf, V. V., 1933. Die Breite der Spektrallinien in Gasen, *Phys. Zeit.*, **34**, 1.
- Woods, R., 1983. in *Molecular Ions: Spectroscopy, Structure, and Chemistry*, North-Holland, Amsterdam, Amsterdam.